# Studies on Metal Chelates

## (Chemical Speciation and Equilibrium Studies of Mixed Chelates)

*A thesis submitted for the Degree of*

*Doctor of Philosophy*

*In*

*SCIENCE*


***Submitted by***

**Ved Prakash Shukla**

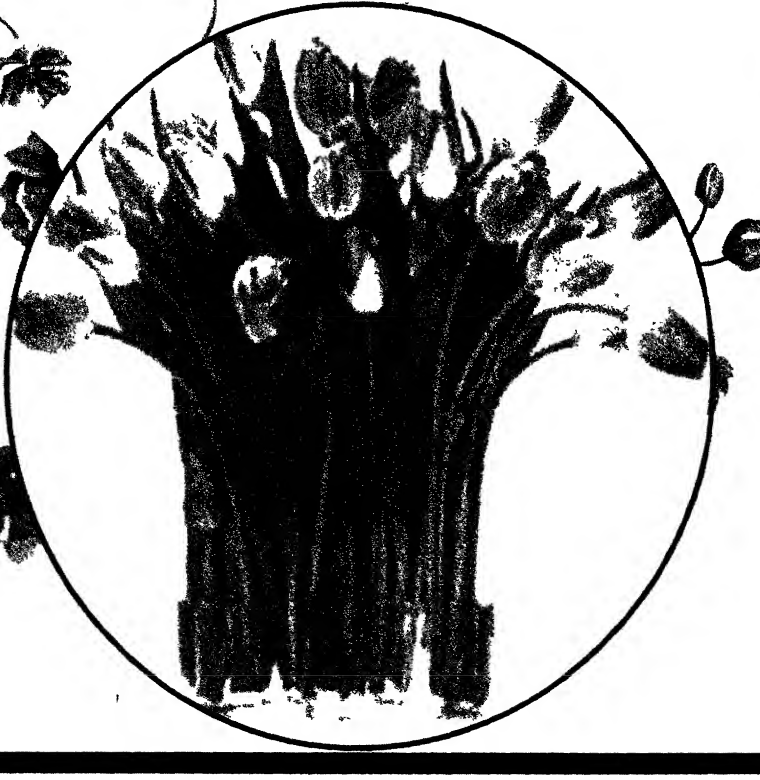
**M.Sc.**


**2007**

Dedicated to

My Beloved Grand Father

Jagdish Prasad Shukla



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## Certificate

*This is to certify that the candidate Mr. Ved Prakash Shukla, has fulfilled all the requirements for the submission of D.Phil. Thesis to the University of Allahabad.*

Dated: 15-05-2007

Place: Allahabad

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Ved Prakash Shukla.

*(Ved Prakash Shukla)*

# *Contents*

# Chapter 1

# *Introduction*

# Introduction

Chelation is the process of reversible binding (complexation) of a ligand - the chelant, chelator, chelating agent, sequestering agent, or complexing agent to a metal ion, forming metal complex, the chelate. It comes from the greek word "chele" introduced by Morgan and Drew[1], in 1920 and was used to designate such cyclic structures which arise from the union of metallic ions with organic or inorganic ligands. The chelating agent must be of low toxicity and not metabolized so as to persist on changes in the biological system to perform their scavenging functions due to their interaction with metal ions to form metal chelates or dislodging the bound metals and excreting these as soluble chelates from the system[2].

The metal chelates play an important role in various fields of biological[3-5],analytical[6-8],industrial[8-11]and medicinal[12] importance. Biological system contains various essential and non-essential or potentially toxic metal ions[13-15] sodium, calcium, manganese, cobalt, copper, zinc, lead, mercury and cadmium, etc . The human body contains many chelating agents[16] such as amino acids, globins, proteins, enzymes, carboxylic acids and nucleic acid-bases, which form chelate compounds with sodium, magnesium, potassium, calcium, manganese, iron, cobalt, copper, zinc, molybdenum, etc. Metal chelates include substances such as haemoglobin, haemocyanin, myoglobin, vitamin $B_{12}$, chlorophyll, nucleic acid and various enzymes[17].

In assemblage of metal ions and ligands, the extent to which any specified kind of metal ion combines with any specified kind of ligand depends

not only on the relative and absolute concentration of all of the kinds of ligand present but also on the relevant pK and formation constant as well as pH of solution .

The present thesis is concerned with the equilibrium study of some ternary and quaternary metal chelates of biological significance. In the present study, the formation of metal complexes of uracil, thymine, lysine, proline, valine and asparagine with a variety of biologically important bivalent transition metal ions viz. cobalt, nickel, copper and zinc has been investigated potentiometrically in the biologically relevant conditions. The relevant stability constants have been calculated using computer technique.

Metal ions are required for the growth of all life forms[18-21]. Currently, about half of all proteins contain metal ions[21] and most ribozymes cannot function without metal ions. In particular transition metals such as cobalt, iron, copper and zinc are involved in many redox processes requiring electron transfer[23].

**Table 1.1 Biological significance and specific effects of metals under study.**

| ELEMENTS | BIOLOGICAL SIGNIFICANCE | SPECIFIC EFFECTS |
|---|---|---|
| **Cobalt (Co)** | **An essential element, occurs in co-enzyme viz. vitamin $B_{12}$ (Cyanocobalamine)** | **Very toxic to plants and mammals. Higher doses of cobalt causes Polycythaemia and hyper-lipaemia, wasting diseases.** |
| **Nickel (Ni)** | **An essential trace element, active metal in several hydrogenase and plant urease. It stabilizes the ribose confirmation.** | **Nickel dust or nickel containing asbestos powder inhaled on occupational exposure may produce bronchial cancer in man.** |
| **Copper (Cu)** | **An essential trace element, active role in metalloenzymes viz. cytochrome 'c' oxidase, haemocyanin.** | **Low concentration of Copper salt may cause vomiting and considerable gastrointestinal irritation in patients, suffering from Willson disease.** |
| **Zinc (Zn)** | **An essential element, contained in several dehydrogenases, aldolases, peptidases, phosphatases and isomerase of yeast .** | **Zinc pollution may causes several respiratory irritation and cynosis called Zinc fume fever.** |

Complexation of metal ions of biologically importance with amino acids, small peptides and their derivatives are of great significance, as many of these systems offer simple models of otherwise complex metal- amino acids equilibria occurring in enzymatic process[24,25]. Mixed chelation occurs commonly in biological fluids[26], as millions of potential ligands are likely to compete for metal ion found in vivo.

Mixed-ligand, mixed-metal complexes involving more than one metal ions of the same or different types may prove as better models for multimetal-multiligand equilibrium occurring in the biological systems. Quaternary complexes play important role in biological system[27]. Such complexes are of importance in the study of bio-fluids particularly when hyper-accumulated metal ions are present for physiological or pathological nature[28]. Mutual influences between metal ions may be of antagonist or of synergistic nature[29]. Model studies with relatively simple molecules of known structure often yield valuable information that gives clues to the roles of metal ions in many enzymic reaction[30,31].

Amino acids are a group of organic compounds containing two functional groups - amino and carboxyl. The amino group ($-NH_2$) is basic while carboxyl group (-COOH ) is acidic in nature. They mostly exist in the ionized form in the biological systems. Amino acids (except Glycine) possesses fair distinct groups[32,33] (R, H, $COO^-$, $NH_3^+$) held by α- carbon . Thus, all the amino acids (except glycine ) have optical isomers . Most of amino acids are soluble in water which shows Zwitter ion in solution. Zwitter ion (or dipolar ion) is a hybrid molecule containing a positive and a negative ionic groups. Chelation through terminal amino groups has been found in the

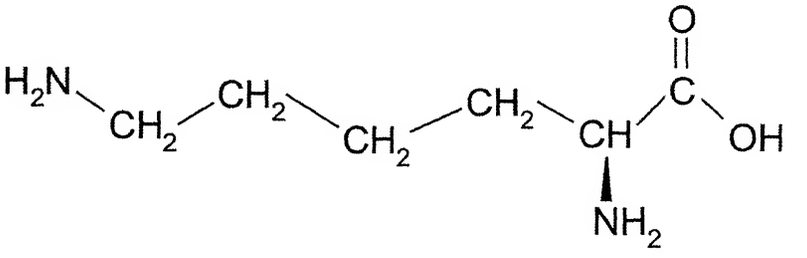
crystal structure of all complexes in which amino acids or peptide function as bidentate or polydentate ligands[34,35]. The details of some amino acids used as ligands are described below.

**LYSINE**

Lysine is an essential, genetically coded amino acid and a basic building block of all proteins. It is important for human health but cannot be manufactured by the body. It is required for growth and bone development in children, assists in calcium absorption, maintaining the correct nitrogen balance in the body and lean body mass. It also plays an essential role in production of the carnitine, a nutrient responsible for converting fatty acids into energy and helping to lower the cholesterol. Furthermore it is needed to produce antibodies, hormones, enzymes, collagen formation, a substance important for bones and connective tissues including skin, tendon, and cartilage, as well as repair of tissues. Lysine is useful for patients recovering from injuries and it might be used in maintaining healthy blood vessels. L-lysine helps to improve the absorption of calcium from the digestive tract and prevent loss of calcium in the urine and also may help to prevent bone loss associated with Oesteoporosis[36].

L-lysine can be used to treat mouth and genital lesions caused by Herpes simplex virus as well as Shigles caused by Herpes Zoster Viruses. Certain forms of Lysine bound to anti-inflammatory medications[38] may help to alleviate pain episiotomy. If it is too little in the diet, kidney stones and other health related problem may develop including fatigue, nausea, agitation, blood shot eyes, slow growth, anemia and reproductive disorder.

Structure of Lysine is shown in fig.



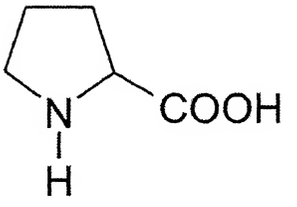
( α, Є- diaminocaproate )

## Proline

L- proline is a non-essential neutral genetically coded amino acid . The widely distributed L-proline is distinguished from all other amino acids, except hydroxyl proline, by its readily solubility in alcohol. In this, -$NH_2$ group is incorporated into a five membered ring. Proline usually functions as bidentate complexing N, O, donor ligand; coordination taking place from one imino and one carboxylato group. Cyclisation of imino nitrogen with the side chain terminal carbon, leads to many of unique properties of proline. This greatly restricts the conformational space available to the peptide in which proline occurs. Other effects are reduced barrier to cis-trans isomers of the peptide bond and a loss of hydrogen bonding capability of the imino nitrogen. These effects give proline a unique role in secondary structure elements in which it occurs. Proline also has role in structural proteins, signal transduction and other areas. Proline is a component of collagen, a major structural component of cells and animals.

According to the review by David Rhodes[38], proline accumulation is a common metabolic responses of higher plant to water deficits and salinity stress. Proline is highly water soluble amino acid and is accumulated by leaves of many halophytic higher plant species grown in saline environments, in leaf tissues and shoot apical meristems of plants experiencing water stress in desiccating pollen, in root apical regions growing at low water potentials and in suspension culture plant cells adopted water stress.

Proline protects membranes and proteins against the adverse effects of higher concentrations of inorganic ions and temperature extreams. Proline may also function as protein compatible hydrotrope and as hydroxyl radical scavenger. Structure of Proline is shown in fig.



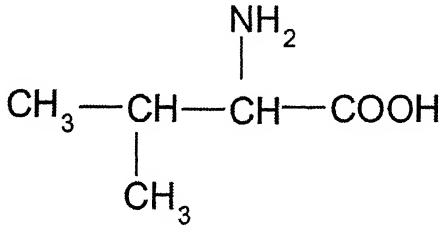

(2-pyrrolidinecarboxylate)

**VALINE**

Valine is one of the several essential amino acids needed in the diet, as the human body synthesize it from simple metabolites. L- valine is a neutral genetically coded amino acid, analogs of arginine and lysine . It is one of 20 most common natural amino acids on the earth and it codes for DNA. Valine contributes to the structure of proteins into which it has been incorporated by the tendency of its side chain to participate in hydrophobic interactions. It is obtained by hydrolysis of protein and was first isolated by the German Chemist Emil Fisher in 1901 from casein[39,40].

Valine has a stimulating effect and is needed for muscle metabolism, repair and growth of tissues and maintaining the nitrogen balance in the body. It can also play an important role in treating reversing hepatic encephalopathy or alcohol related brain damage as was in degenerate neurological conditions.

Maple Syrup Urine Disease (MSUD) is caused by the inability to metabolize leucine, Isoleucine and valine. The disease is so named because urine from affected people smells like maple syrup. Very high levels of Valine can cause symptoms such as a crawling sensation on the skin as well as hallucinations. Structure of valine is shown in fig.



(α – aminoisovaerate)

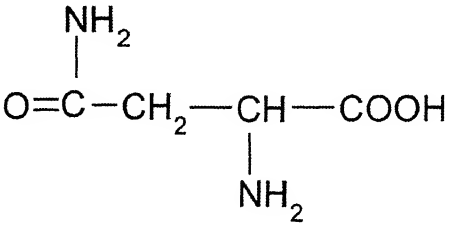
**ASPARAGINE**

Asparagine is a non-essential amino acid, is closely related to aspartic acid and can be manufactured from this nutrient. It was first isolated in 1932 from Asparagus for which it was so named. It is widely available in plant protein and is a constituent of plant tissue. It has carboxamide as the side chain's functional group[41]. This is β-amide of aspartic acid and has been isolated from proteins after enzymic hydrolysis.

It is manufactured from other amino acids in the liver, it does not have to be obtained directly through the diet. Asparagine has a high propensity

to hydrogen bond, since the amide group can accept two and donate two hydrogen bonds. It is found on the surface as well as buried within proteins.

Asparagine provides key side for N-linked glycosylation, modification of the protein chain with the addition of carbohydrate chains. It is required by the nervous system to maintain equilibrium and is also required for amino acid transformation from one form to the other which is achieved in the liver. Structure of Asparagine is shown in fig.



(β-amide α-aminosuccinate)

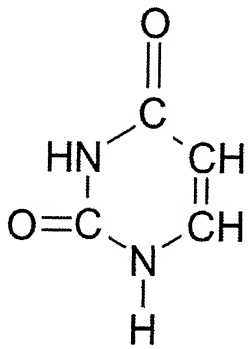
The properties to store, express, transmit genetic information and to undergo mutation[42] depends upon the chemical characteristics of a class of substances known as nucleic acids, which present in every living cell as well as in viruses and bacteriophages. The nucleic acids constitute, infact, the essential substance of genes and the apparatus by which the genes act. Nucleic acid falls into two principle classes according to the nature of sugar they contain, DNA (deoxyribonucleic acid )[43] and RNA (ribonucleic acid).

**URACIL**

Uracil is a pyrimidine base which is common and naturally occurring[44]. Uracil was isolated by hydrolysis of yeast nuclein[45,46] that was found in bovine thymus and spleen, herring sperm and wheat germ[47]. Uracil is a planar, unsaturated compound that has the ability to absorb light[48]. It is found in RNA, it base pairs with adenine and is replaced by thymine in DNA. It is methylated

into thymine to protect the DNA and to improve the efficiency of DNA duplication. It readily pairs with adenine because the methyl group is repelled into a fixed position. Uracil pairs with adenosine through hydrogen bonding. Uracil can also bind with a ribose sugar to form a ribonucleotide, Uridine.

Uracil can be used for drug delivery and as a pharmaceutical. 5-flourouracil is an anti-cancer drug (antimetabolite) used to masquerade as uracil during the nucleic acid replication process. Uracil's use in the body is to help carry out the synthesis of many enzymes necessary for cell function through body with riboses and phosphates. Uracil serves as allosteric regulator and coenzyme for reaction in the human body and in plants[49]. Uracil also involves in biosynthesis of polysaccharides and transportation of sugar containing aldehydes. Uracil can be used to determine microbial contamination of tomatoes. Its derivatives are used in pesticides. It is also used as an anti-photosynthetic herbicides and destroys weed[50]. Structure of Uracil is shown in fig.



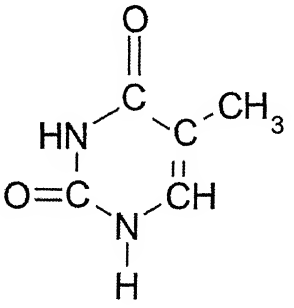

(2,4-dioxopyrimidine)

**THYMINE**

Thymine is an organic base of the pyrimidine family. It is also known as 5-methyl uracil, as the name indicates thymine may be derived from the methylation[51,52] of Uracil at the 5$^{th}$-carbon .

Thymine is found in the nucleic acid DNA. Its molecular structure contains two heterocyclic nitrogen[53,54] atoms at position 1,3 and it can exist in two or more tautomeric forms (Lactam and Lactim). In RNA, thymine is replaced with Uracil in most cases. Thymine combined with deoxyribose creates the nucleosides deoxythymidine, it can be phosphorylated with one to three phosphoric acid groups and forms the three nucleotides respectively TMP (thymidine monophosphate), TDP (thymidine diphosphate) and TTP ( thymidine triphosphate) . The TTP can donate one of its phosphate groups to adenosine diphosphate (ADP) to form adenosine triphosphate (ATP) .Since the thymidine nucleotides contain only deoxyribose and not ribose so, TTP is the source of thymidine in RNA.

Thymine involves biosynthesis of DNA, it preserves and transfers genetic information. It could also be a target for actions of 5-Fu in cancer treatment. 5-Fu can be metabolic analogue (in DNA synthesis) or uracil (in RNA synthesis). One of the common nutrition in DNA involves two adjacent thymines or cytosine , which in presence of UV light may form thymine dimers, causing " Kinks " in a DNA molecule that inhibit normal function . Structure of Thymine is shown in fig.



(5-methyl-2, 4-dioxopyrimidine)

## Present work

The present work describes the chemical speciation and formation equilibria of ternary and quaternary chelates of bivalent cobalt, nickel, copper, and zinc transition metal ions involving the following combination of ligands.

(A) Lysine-Uracil

(B) Proline-Uracil

(C) Valine- Thymine

(D) Asparagine-Thymine.

The formation has been studied potentiometrically by Irving and Rossotti technique[55] at biologically relevant conditions. Complexation equilibria have been derived on the basis of distribution curves of complexes occurring at different pH. The $\beta_{pqrst}$ values were evaluated using SCOGS Computer Program[56]. The result of these studies have been described in chapters IV and V. Chapter II deals with the brief survey of metal chelates with special reference to mixed chelation, whereas Chapter III contains the theoretical treatment and experimental details. The conclusions arrived on given in the last Chapter and the references are listed at the end of the thesis.

# Chapter 2

# *Literature Survey*

## *(A Brief Review)*

# LITERATURE SURVEY

The complexation of polynuclear metal chelates have been topic of growing interest in the study of mixed chelation .The mixed chelates are likely to be important as the active involvement of metal ions in the multimetal - multiligand equilibria in biological system. Metal complexes comprising one metal or ion and two different ligands is termed as mixed chelates whereas a system comprising two metal atoms or ions and two different ligands are termed as multimetal - multiligand system. Mixed ligand complexes have been extensively studied during the last two decades. For the investigation of mixed ligand complexes in solution, waters [57] used the ligand displacement method[58]. Bennett[59] studied Copper(II) ethylenediamine-aminodiacetic acid chelates and underlined the role of entropy in the form of mixed chelates.

Multimetal-multiligand equilibria are very common in enzymatic process and therefore mixed-metal, mixed-ligand complexes may prove as better model for such equilibria occurring in the biological system. Mukherjee and Bandyopadhyay[60] described the results of the equilibrium study on the mixed ligand complex formation of Iron (III) with boric acid in presence of nitrilotriacetic acid and anthranilic acid in aqueous solution by Potentiometrically. J. M. Tercero – Moreno, A. Mathilla – Hernandez and J. Niclos – Guthierrez[61] conducted studies on Cu(II) and Ni(II) chelates with dihydrogen trans – 1 , 2 diaminocyclohexane – N , N , $N^1$ , $N^1$ –

tetraacetate$^{2-}$ ion, $H_2CDTA^{2-}$ synthesis , XRD structure and properties of ( Cu ( $H_2CDTA$ ).$H_2O$ and (Ni ($H_2CDTA$)($H_2O$).4$H_2O$.

Bhattacharya and Banerjee[62] observed the formation and equilibria of the ternary complex of nitrilotriacetoferrate (III) with 2,2,-bipyridyl in aqueous solutions . Farkash et. al.[63] studied the coordination modes of hydroxamic acids in Cu(II) , Ni(II) and Zn(II) mixed ligand complexes in aqueous solution by using Potentiometry. Ch Agoston et al.[64] examined stability constants and structure of complexes of Cu(II), Ni(II), Zn(II), CO(II) and Cd(II) with L-cystein glycinedisulfide by potentiometric and various spectroscopic techniques. Kurzak et al.[65] determined stability constants of Co(II), Ni(II) and Mn(II) complexes with some aminodiphosphonic acids in aqueous medium by Potentiometry and Spectrophotometry. Remelli et. al.[66] investigated the complexation equilibria of some dipeptides with the Cu(II) ions in aqueous solution . Protonation and Complex formation constants have been determined by Potentiometric method.

E. Farkas et al.[67] , discussed coordination modes of hydroxamic acids in Cu (II) , Ni( II ) and Zn ( II) mixed ligand complexes in aqueous solution by pH-metric, spetrophotometric , EPR and calorimetric methods . Chiara Conato et. al.[68] observed Ni(II) complexes of dipepeptides a thermodynamic and spectroscopic study . Kurzak et. al.[69] observed stability of the mixed ligand Cu(II) complexes with diethylenetriamine and histidine or methioninehydroxamic acids in water solution .

Planka et. al.[70] performed an ESR study of Cu(II) Glycyl-L-serine and Cu(II)-L-seryl-glycine systems by the simultaneous analysis of

multicomponent isotropic spectra. They also studied formation constants and their coordination modes. Dallavalle and his coworkers[71] studied the formation equilibria of ternary complexes of Cu(II) with (S)- tryptophan hydroxamic acid and both D-, L-amino acid in aqueous medium by Potentiometric and Spectrophotometric method . Visser and Bason[72] investigated the crystal structure of $CS_2$[ Co(NTA) ($CO_3$)] $H_2O$ from X-ray diffraction data . Kroczewska et. al.[73] studies stabilities of the mixed ligand complexes of Cu(II) ion with N,N,N,N,N-penta methylene triamine [ N,N,N,N,N-penta methyl –{bis (2- amino ethyl) amine } mesdiene] as primary ligand and α- alanine hydroxamic acid [2-amino-N-hydroxypropanamide, α-alpha ] or β- alanine hydroxamic acid [ 3-amino-N hydroxypropanamide, β-alpha] as secondary ligand and their absorption, EPR spectra at various pH values .

Dobrzynska et al.[74] have investigated the synthesis and structure of mixed ligand complexes of Cu(II), bis( 9,10-dihydro- 9- oxo-10-acridineacetato ) bis (imidazole) Cu(II) tetrahydrate. Equilibrium studies on Cd(II) and Zn(II) chelates of mercaptocarboxylic acids have been under taken by Crisponi et. al.[75]

Q.D.Liv et. al.[76] observed the lanthanide contraction and anions controlled dimensional diversity in Ln-Cu-NTA ( Ln = Lanthanide , $H_3NTA$ =Nitrilotriacetic acid) Coordination polymers. A series of Lanthanide - Cu(II) coordination polymers with $H_3NTA$ were sythesised in aqueous solution and their crystal structures were determined. Miranda and Judit[77] determined the possibility of occurrence of biological relevant guanidino-carboxylate interactions was investigated in ternary system involving

guanidine acetic acid (Gaa) and glutamic acid(Glu) , aspartic acid (Asp) or glycine (Gly) with Cu(II) metal ion .The study was done in solution using Potentiometry and observed their stability constant.

Garcia-Raso and his coworkers[78] suggested crystal structure of the Cu(II) ternary complex of N-salicylidene-L-serinato with 2,6-diaminopyridine and observed the toxic studies against Drosophila melanogaster. Ijeri and Srivastava[79] studied the complexation of macrocyclic compounds with mono, di and trivalent transition and heavy metal ions in 90% (V/V) DMSO + water medium. Stability constants for such complexes were elucidated by Conductometric and Potentiometric methods. The limiting molar conductivities of metal ions and complexes were also determined. Gunnlaugsson et. al.[80] have determined the studies on the synthesis structural and biological evaluation of glyala based lanthanide macrocyclic conjugates as supramolecular ribonuclease mimics. R. Ettorre[81] investigated the complexes of Palladium (II) with Adenosine has been shown to bind to diethylenetriamine Palladium (II) in aqueous medium through N-1 and N-7sites.

D.N. Shelke[82] described equilibrium study of the mixed ligand complexes of copper (II)-aminoacids and 2, 2'-bipyridyl with thiodicarboxylic and pyridine dicarboxylic acids. Khatel et.al[83] studied the effect of mixed ligand complex in the ionization of pyrrole hydrogen of histidine and histamine. Ionic stability constants were calculated for malates, citrates and the specific rotation was determined by optical rotation.

Mahmoud, M. A. Mohamed, M. Shoukry[84] studied complex formation equilibria of Palladium (II) complexes involving N,N$^1$–dimethylenediamine,

DNA constituents and cyclobutane dicarboxylic acid. The catalysis of Glycine methyl ester hydrolysis through complex formation. Alfonso Fernandez –Botello, Antonin Holy, Virtudes, Moreno, H. Sigel[85] described Stability and structute of binary and ternary metal ion complexes in aqueous solution of the Quaternary 1- (2- ( Phosphonomethoxy)ethyl) derivative of 2,4-diaminopyrimidine (PMEDA) $Py^{-}$ properties of an acyclic Nucleotide analogue by potentiometric titration in aqueous media and also studied about biological activity of nucleotide analogue .

The formation of hetroligand chelates of some transition metals, DTPA as primary ligand and diamine as the secondary ligand using potentiometry and specrophotometry have also been studied in solution equilibria[86,87]. Nigam et.al.[88,89] studied the electrode behavior of Cu(II)-mixed ligand complexes at the dropping Hg electrode and correlated the spectral and redox properties.

Dey et al.[90] determined the stability constant of Cu(II), Ni(II), Co(II), Zn(II) and Mn (II) complexes with 1,10 phenanthroline as primary ligand and adenine, mercaptopurine, thioguanine, xanthine, hypoxanthine, guanosine and xanthosine as secondary ligand .Taqui Khan et. al[91-93] studied the formation of some mixed ligand ternary complexes with adenine, cytosine, uracil, thymine, xanthosine, and hypoxanthosine as primary ligands and 1, 10 phenanthroline, 2,2, dipyridyl sulfosalicylic acid and N, $N^{1}$ tetramethyl-ethylene diamine as secondary ligands .

Nair[94] investigated the stability constant of ternary complexes of Cu (II), Zn(II)with Glycine and Imidazole, histamine or L- histidine . Ramanujam et. al.[95-96] described the formation constant of various Cu (II),

Ramanujam et. al.[95-96] described the formation constant of various Cu (II), Ni (II), and Zn(II) mixed ligand chelates. The stability constants are compared and discussed in the terms of basicity size of the chelate ring, charge nertralization and statistical consideration. The formation of mixed ligand complexes with heterodonar atoms are favoured as compared to mixed ligand complex with identical donar atoms. Nigam and Srivastava[97] studied the formation of some mixed ligand transition metal complexes of Uracil and thymine with aspartic acid and glutamic acid as primary ligand.

R. G. Bhattacharyya and (Mrs) I. Bhaduri[98] have been isolated complexes metal with constituents of nucleic acid and characterized by Analytical, Infrared and TGA data. They also discussed possibility of coordination from N(3) and N(9) atoms in nucleic acid constituents. M. S. Nair et. al.[99] investigated ternary Coordination complexes of Cu(II) with L-histidine and some selected amino acids , by pH titrimetry in aqueous perchlorate media .

Leporati[100] determined formation and stability of ternary Cu(II)-edma aminoacid systems, where edma refers to ethylenediamine-N- acetate and amino acid to Glycine (gly) , L-alanine (ala ), L-norvaline (nor), L-phenylalanine (phe) or L- tryptophan (trp) Potentiometrically . Nair[101] insvestigated stability and structure of some binary and mixed ligand complexes of Zn(II) for ternary chelates . Nair et. al.[102-104] described the heterobinuclear complex formation of (i) iminodiacetic acetic acid (imda) with Cu(II)-Ni(II) and Ni(II)-Zn(II) and (ii) DL-2,3- diaminopropionic acid (dapa) with Cu(II)-Ni(II) and Cu(II)-Zn(II). In other study they reported the mixed metal complex formation of (i) L-aspartic(aspt) and with Cu(II)-Ni(II)

, Cu(II)-Zn(II) and Ni(II)-Zn (II) (ii) DL-4- amino-3- hydroxybutyric acid (ahba) with Cu(II)-Ni(II) and Ni(II)-Zn(II) and of (iii) L-2-4- diaminobutyric (daba) with Cu(II)-Ni(II) and Cu(II)- Zn(II). In the continuation of their earlier work on mixed – metal complex systems, they reported the heterobinuclear complex formation of (i) dapa (i) dopamine (dopm)and (iii) L-Histidine (his) with Cu(II)-Ni(II), Cu(II)-Zn(II) and Ni(II)-Zn(II) and (iv) L-cysteine (cys) and ((v) D- penicillamine with Ni (II)- Zn(II) in aqueous solution .

Mukherjee and Ghosh[105] obtained the interaction of metal ions viz- Co(II), Ni(II), Cu(II), and Zn(II) with 6 amino pencillanic acid as the primary ligand , bipyridine , glycinate and imidazole as secondary ligands. Mukherjee and Ghosh[106] with a view to elucidate the varied mode of binding of ampicilin, described a combined potentiometry and spectrophotometry on the mixed ligand complex formation of Co(II), Ni(II), Cu(II) and Zn(II) with ampicilin and amino acids viz. , glycinate, α-alaninate, β-alaninate and aspartate in aqueous solution at 37°C at a fixed ionic strength.Patel et al.[107] have described proton ligand constants for two peptides (glycyl alanine and glycyl valine) and three imidazoles (imidazole, 2-methylimidazole and 2-ethylimidazole) hydrolytic constants for three metal ions Cu(II) : (GA/GV) : TMH(1:1:1) )with respect to different imidazoles have been evaluated , and the observed order has been explained in terms of electronic and molecular structure of the alkyl substitutents.

Mukherjee and Basu[108] observed the mixed-ligand complex formation equilibria of $M^{2+}$ions (M=Co, Ni, Cu and Zn) with sulfapyridine, sulfadiazine and sulpfathiazole as primary ligands and glycine β-alanine and

DL- methionine as secondary ligands. The work aimed to elucidate the modes of coordination of the sulfa drugs to $M^{2+}$ ions in the presence of the aminoacid ligands with a view to see the effect of size of the chelate rings, steric crowding metal- ligand π-interactions, hydrogen bonding and ligand stacking intractions on the structure and stability of the mixed ligand , metal drugs , amino-acetate complexes formed in solution.

Patel and Pandey[110] studied synthesis of an imidazole bridged heterometallic binuclear Cu-Zn complex of ternary metal complex of Glycylglycine. Its variable pH visible spectra (50 % DMSO) and X-ray band EPR spectra in frozen solution have also been studied.

Single crystal X-ray diffraction has been used to structurally characterized a limited number of ternary metal complex containing NTA and NTA derivatives. Only few crystal structures of the general forms M(NTA) (amino acid) however, have been reported namely Co-NTA-Phenylalanine, Co-NTA-leucine and Co-NTA Glycine[111]. Nair et.al.[112,113] observed studies on some Cu(II) ternary complex system of biological significance, described Potentiometric study of multiple equilibria in Ni(II) and Cu(II) mixed ligand comlplexes containing nicotinic acid imidazoles.

In another study they investigated[114] solution behaviour of mixed ligand complexes of Ni(II) involving Penicillin group drugs and Sulphur containing ligands under physiological conditions . Nair and Subbalakshmi[115] have done pH-metric and electronic spectral measurements on the mixed ligand complexes of Cu(II) containing unsubstituted imidazole and some dipeptides .Nair and Neelakantan[116] have investigated the results of multiple equilibrium studies involved in the Ni(II) – ampicillin and some

potentially bi- and tri- dentate ligands , viz. 1,2- diamino propane 1,3-diamino propane, DL-2,3-diamino propionic acid , DL-2,4 diamino butyric acid and DL-2,5- diamino valeric acid. In all these system, in the NiAB species, the binding ligands A and B was similar to their binding in their respective binary systems.

Nair and David[117] in continuation of their earlier work on the solution equilibria of Schiff base complexes of transition metal ion reported the solution equilibria involved in the Co(II) / Ni(II) / Cu(II) / Zn(II) -2-Pyridine carboxyl aldehyde (A) L-threonine and L-glutamine (B) systems. They demonstrated the formation of Schiff base complexes stiochiometry MAB, $MA_2B$ and $MA_2B_2$. Mukherjee and Das[118] obtained the result of equilibrium study on the complex formation of boric acid with cis-diaqua Cobalt (III) complexes. The result indicated the predominant formation of binuclear mixed ligand borate complexes $[(N_4)Co(BO_4)Co(N_4)]^+$ over the mononuclear$[(N_4)\ Co(H_2SO_4)]$ complexes.

Kumar and Nayan[119] discussed the quantitative equilibrium studies on mixed ligand complexes of Nickel(II) , Copper(II) and Zinc(II) with some nitrogen and oxygen donar ligands. Varshney and Gupta[200] have investigated Potentiometric studies on mixed ligand complexes of La(III), Sm(III), Eu(III) and Dy(III) with cis-1,2,3,4,-cyclopentane tetracarboxylic acid (CPTA) as a primary ligand and D-L-methionine as secondary ligand. The studies show formation of ternary complexes having (1:1:1) ternary system. The thermodynamic parameter for the ternary complexation have also been evaluated. Patel et al.[121] observed equilibrium study on the formation and stability of mixed-ligand, mixed-metal complexes of Copper (II), Nickel (II),

and Zinc(II) with Pentamethyldiethylene and Imidazole. Mukherjee and Das[122], investigated mixed ligand complex formation of Co(II), Ni(II) and Zn(II) with boric acid and some (N,N) bidentate ligands. V.Mishra[123] synthesized mixed ligand chelates of some multidentate heterocycles with Co(II) and Ni(II) imides.

Ghosh et al.[124] studied mixed ligand oxovanadium (IV) complexes with two different types of bidentate ligand have been prepared and characterized by elemental analysis, IR , EPR and UV-Visible spectroscopies. B. S. Garg, Poonam Dwivedi[125] observed solution studies on ternary complex formation of bivalent metal ions with cephalexin and aminoacid acids, ß-alanine and cysteine. Bing and his coworkers[126] reported the synthesis and application of nitrilotriacetic acid and modified magnetic nanoparticles that can act as a general agent to separate transport and anchor a protein. Taqui Khan and Ch. A. Lincoln[127] studied binary and ternary nucleoside complexes of bivalent metal ions in solution. R. M. Raju and V. A. Pannala[128] determined complexation behaviour of Mercuric(II) acetate towards nucleobases. D. Kumar et al.[129] observed equilibrium studies on binary and ternary complexes of Palladium and Cadmium with some nitrogen and oxygen donar ligands.

Kushwaha and Neeta Verma[130] observed solution study of Copper(II)-dipeptide complexation with tyrosinate and lysinate as bridging residues. Halli and Shashidhar[131] described stability constants of some bivalent metal ions with Naphthofuran-2-carbohydrazide Schiff base. Krishna et al. used mercury-DTPA as a ligand and thoroughly studied a variety of mixed metal complexes [132-135]. P.G. More, B. N. Muthal and Mrs. A. S. Lawand[136]

investigated complex formation of some transition metals with thiazole Schiff bases. The thermodynamic parameters ($\Delta G$ , $\Delta H$ and $\Delta S$) at different temperatures have been calculated. G. N. Rao and A. Ramkrishna[137] determined speciation of ternary complexes of Cobalt(II) and Nickel(II) with L-glutamine and succinic acid in urea water mixtures by Potentiometry. S.S.Sanjay and S.S.Narvi[138] studied the formation of mixed ligand complexes of Copper (II), Nickel(II), Cobalt(II) and Zinc(II) with nitrilotriacetic acid as primary ligand and Uracil, Thymine, 2-Thio uracil as secondary ligand.

R. Kaur and B.S. Sekhon[139] observed stability constant of 5–carboxyuracil and 5 –carboxy-2-thiouracil with some metal ions by Potentiometric titration technique. The correlation between stability constant and various parameters relating to ligand as well as metal are discussed. Reddy et.al.[140] investigated equilibrium studies on ternary chelates of trivalent metal ions with 2-(2-hydroxy Phenyl) benzimidazole, 2-(2-hydroxy phenyl) benzoxazole and other ligands in solution.

Krishna and his co workers[141-147] extensively studied mixed ligand-mixed metal and multimetal multiligand complex formation with certain amino poly carboxylic acid in aqueous solution. They observed the stability constants of complexes by certain techniques. Krishna et al. measured the metal-ligand bond length in some simple and mixed Cu(II) amino acid chelates from X-ray K-absorption fine structure[148].

Bhattacharya et al.[149] determined stability constants of homobinuclear Cu(II) complexes of some dinucleating ligands, having equivalent (N-O) coordinating sites, viz. 4,4′ -di(O-hydroxy benzyl ) diamino diphenyl

methane ($H_3A^{1'}$) and 4,4′ -di(O-hydroxy benzyl ) diamino diphenyl ether ($H_3A^{2'}$) and mixed ligand Cu(II) complexes with one of the above ligands and bipyridyl, glycine, α-alanine, phenylalanine, lyrosine or tryptophan as secondary ligands, have been determined potentiometrically in (50:50, v/v) water-dioxane medium using a computer program.

Chakravarty et al.[150] studied the formation of thiocyano bridged dinuclear ruthenium (III) complex ion by the reaction between thiocyanatopentaamine ruthenium (III) and aqua pentaamine ruthenium (III) complex ion in aqueous solution.Chakravarty and his coworkers[151] observed the equilibrium studies of ternary chelates of some divalent metal ions with cephaloporins and α-alanine.

# Chapter 3

# *Experimental*

# Experimental

Evaluation of the solution properties which changes as a result of chelate formation can give information on the stability and existence of different species[152]. To choose an adequate experimental method is prerequisite for obtaining reliable formation constants.

It has been proved that electroanalytical techniques known so far, pH metery is still one of the most important methods to study the complexation equilibria of interaction of metal ion and ligands[153]. Whereas electrode potential studies involving the measurement of $H^+$ ions in complexation or chelation by a protonated ligand where there is a liberation of hydrogen ion as a consequence of the reaction. In such cases glass electrode may be used to furnish information on the $H^+$ ion concentration as well as on the extent of complex formation.

Investigation in solution exhibit the interest of the chemist both kinetic and thermodynamic aspects, while the kinetic approach of a complex species refers to the speed with the transformation leading to the attainment of the equilibrium takes place, the thermodynamic aspects concern itself to the extent to which this species will form or be transformed into another species. Under certain conditions, when the system has attained equilibrium the work is reported in recent years in the field of equilibrium chemistry. It is not merely concerned with the collection of bulk of equilibrium data but elaborate theoretical treatments towards elucidation of metal-ligand interaction in solution have also carried out. An immense amount of equilibrium data is available in different volumes is published by Martell[154], Sillen[155] and Smith [156].

## THEORETICAL PRINCIPLE

The concept of stability constant in chemical equilibrium between a metal ion 'M' and a ligand 'L' in solution was introduced by Abegg[157] and Bodlander[158-159] for a reaction of type.

$$M_{(g)} + nL_{(g)} \rightleftharpoons ML_{n(g)} \qquad \text{.....(3.1)}$$

Formation of complex in solution proceeds by the stepwise addition of the ligands to the metal ion, a number of successive equilibria can be formulated. The above equilibrium may generally be written in a more convenient form as,

$$\begin{aligned} M + L &\rightleftharpoons ML \\ ML + L &\rightleftharpoons ML_2 \\ ML_2 + L &\rightleftharpoons ML_3 \\ ML_{n-1} + L &\rightleftharpoons ML_n \end{aligned} \qquad \text{..... (3.2)}$$

From Law of Mass Action,

$$K_1 = \frac{[ML]}{[M]\,[L]}$$

$$K_2 = \frac{[ML_2]}{[ML]\,[L]}$$

$$K_3 = \frac{[ML_3]}{[ML_2]\,[L]} \qquad \text{..... (3.3)}$$

$$\vdots \qquad\qquad \vdots$$

$$K_n = \frac{[ML_n]}{[ML_{n-1}]\,[L]}$$

Where n represents the coordination number of the metal ions, terms in bracket [ ] refers to the activities of different species and

$K_1$, $K_2$, $K_3$.....$K_n$ are thermodynamic stepwise stability constant or formation constant.

$$\beta n = \frac{[ML_n]}{[M]\,[L]^n} \qquad \text{..... (3.4)}$$

where, βn (overall stability constant) is the product of stepwise formation constant ($K_1$, $K_2$, $K_3$,.....$K_n$).

The protonation of the ligand L occurs in steps exactly in the same way as complexation reaction consequently following proton ligand equilibria may be considered.

$$\begin{aligned} L + H &\rightleftharpoons HL \\ HL + H &\rightleftharpoons H_2L \\ H_2L + H &\rightleftharpoons H_3L \\ &\vdots \qquad\qquad \vdots \\ H_{n-1}L + H &\rightleftharpoons H_nL \end{aligned} \qquad \text{..... (3.5)}$$

Using concentrations instead of activities, the stiochiometric proton ligand stability constants are given by,

$$K_1^H = \frac{[HL]}{[H]\,[L]}$$

$$K_2^H = \frac{[H_2L]}{[HL]\,[H]}$$

$$K_3^H = \frac{[H_3L]}{[H_2L]\,[H]}$$

$$K_n^H = \frac{[H_nL]}{[H_{n-1}L]\,[H]} \qquad \ldots\ldots\ldots\ldots (3.6)$$

Hence $\beta n^H$, the overall proton ligand stability constant is determined by,

$$\beta_n^H = \frac{[H_nL]}{[H]^n\,[H_{n-1}L]} \qquad \ldots\ldots\ldots\ldots (3.7)$$

The formation of mixed ligand (Ternary) and multimetal-multiligand (Quaternary) complexes can be considered to take place as follows:

$$M + L_1 + L_2 \rightleftharpoons ML_1L_2$$

$$\beta_{ML\,1L2} = \frac{[ML_1L_2]}{[M]\,[L_1]\,[L_2]} \qquad \ldots\ldots\ldots\ldots (3.8)$$

$$M_1L_1L_2 + M_2 \rightleftharpoons M_1M_2L_1L_2$$

$$\beta_{M1M2L1L2} = \frac{[M_1M_2L_1L_2]}{[M_1L_1L_2]\,[M_2]} \qquad \ldots\ldots\ldots (3.9)$$

$$M_1 + M_2 + L_1 + L_2 \rightleftharpoons M_1M_2L_1L_2$$

$$\beta_{M1M2L1L2} = \frac{[M_1M_2L_1L_2]}{[M_1]\,[M_2]\,[L_1]\,[L_2]} \quad \text{.....(3.10)}$$

Calvin-Bjerrum's[160,161], pH titration technique for calculation of stability constant was adopted by Irving and Rossoti[162]. The importance of Irving and Rossoti's method lies infect that in it the same set of experiments were utilized for the evaluation of acid dissociation constants of the ligand and stability constant or formation constant of the complexes. Accordingly, for binary systems, three mixtures A(Acid), B(Ligand) and C (Complex) free standard sodium and potassium hydroxide solution using a pH meter . Thus, three titration curves were obtained and from the shift of the pH titration curve the value of nH, n, pL are calculated as:

$$\bar{n}H = \{ YTCL_0 - \frac{(N^0+E^0)\,(V_2-V_1)}{(V_0+V_1)} / TCL_0 \} \text{.....(3.11)}$$

Similarly, **n** values were evaluated by the equation,

$$\bar{n} = \frac{(N^0+E^0)\,(V_3-V_2)}{(V_0+V_1) \times \bar{n}H \times TCM_0} \quad \text{.....(3.12)}$$

and pL was calculated by the equation from the equation,

$$pL = \log \frac{K_1[H^+] + K_1K_2[H^+]^2 + \_\_\_}{TCL_0 - \bar{n} \times TCM_0)} X \frac{V_0+V_3}{V_0} \quad \text{..... (3.13)}$$

The stability constant for the system mentioned above had been calculated using the formula:

$\log K = \{\log (TCL_0 \times \bar{n}) - \log (TCM_0)(1-\bar{n}) + pL\}$ .....(3.14)

Where ,

$\bar{n}H$ = Average number of protons attached to the ligand

Y = Number of dissociable or replaceable protons attached to the ligand

$TCL_0$ = Total concentration of the ligand

$N^0$= Concentration of alkali

$E^0$ = Total concentration of free acid

$V_1$= Volume of alkali needed to reach a specified pH for solution 'A' (i.e. Acid)

$V_0$= The total volume of reaction mixture

$\bar{n}$= Average number of ligands attached per metal ion

$V_2$=Volume of alkali required to attain the same pH in the (acid +ligand ) curves

$V_3$= Volume of alkali required to attain the same pH in the (acid +ligand+metal) curves

$TCM_0$= Total concentration of metal present in solution

$K_1^H$, $K_2^H$. $K_3^H$ = Protonation constants of the ligands

$H^+$= Hydrogen ion concentration

$\log (TCL_0 \times \bar{n})$ = The amount of complex formed

$\log \{TCM_0 \times (1- \bar{n})\}$= The amount of free metal ion

pL= The concentration of free ligand

For evaluation of stability constants by the SCOGS computer program[56] in a system of the two different metal ions $M_1$ and $M_2$ and two different ligands A and B in aqueous solution complex formation may be described according to equilibrium.

$pM_1 + qM_2 + rA + sB + t(OH) = (M_1)p\ (M_2)q\ (A)r\ (B)s\ (OH)t$

The overall stability constant ($\beta_{pqrst}$) defined as

$$\beta_{pqrst} = \frac{[(M_1)p\ (M_2)q\ (A)r\ (B)s\ (OH)t]}{[M_1]^p\ [M_2]^q\ [A]^r\ [B]^s\ [OH]^t} \qquad \text{.....(3.15)}$$

may be used to calculate the species distribution curves that provides the clues for the formation equilibria of the complexes.

## COMPUTER PROGRAMS

A computational method has revolutionized the calculation and determination of formation constant or stability constant from equilibrium data, for system containing the ions of upto two metals and upto two ligands. The computer program described in literature[163] employ various strategies and involve a number of methods for data processing.

The earliest computer applications to chemical equilibria studies were concerned with gas mixtures initially using mass valence equation but more recently being designed to seek minimum values for the free energies or

chemical potentials[164]. Programs for the treatment of equilibria in aqueous system developed independently.

The computer program used in employing the "LETAGROP" or "Pit mapping" approach[165-167] by Sillen and coworkers. In 1962 Ingri & Sillen[168] described the program KUSKA for calculating the composition of solutions containing one kind of metal ion & one kind of ligand. The General Computer Program used by Rush, Johnson and Kraus[169] and by Tobia [170] which was called GAUSS has proved very useful in calculating the equilibrium constant of various of species present in solution containing one metal and one ligand.

Anderegg[171] published a similar program that could deal with protonated hydrolysed or polynuclear metal complexes, Ropers and Viovy [172] described a computer program for one kind of metal ion and two different complexing agents including the possibility of mixed complex formation. Three year later a program used to obtain equilibrium concentration in a system comprising three kinds of metal ions and four different ligands.

HALTAFALL[173], a program developed for calculation of equilibrium concentration of all ionic species in mixture of any number of component. The computer program COSMICS (concentration of metal ions and complex species) is designed to deal with all type of metal complex equilibria such as mixed ligand mixed metal species.

Bellome et. al. [174] has been also reported a computer program for calculation of stability constant [175-177] of mono nuclear complexing systems. The program MINIQUAD has been used to evaluate formation constants of species in solution equilibria from data obtained by potentiometric titration.

Extension to system the computer program MINIQUAD used to calculate stability constants of species in solution equilibria from data obtained by pH metric titration. Now developed a new program SUPERQUAD[178] which has been designed a SUPERCEDE. MINIQUAD by providing the facilities, identified above in addition to those offered previously.

Sayce[568] developed a new computer program SCOGS (Stability constant of generalized species) which employs the conventional non linear least square approach. The program is written in FORTRAN IV. It is capable of calculating simultaneously or individually , association constants for any of the species formed in the system containing upto two metal and two ligand, provided that the degree of complex formation is pH-dependent. Thus, SCOGS like ,GAUSS, may be used to analyse appropriate pH titration data to yield metal ion hydrolytic constants, stability constants of simple complexes (ML, $ML_2$ etc.) and stability constant of polynuclear species ($M_2L_3$ , $M_3L_4H$ , $M_2L_2OH$ etc. )

In addition SCOGS may be used to calculate constants for mixed complexes containing two different metals of two different ligands. For a mixture of two metal $M_1$, $M_2$ and two ligands $L_1$, $L_2$, association constants may in principle be calculated with the program for any species which can be described by the general formula.

$M_{1\ M1j} M_{2\ M2j} L_{1\ L1j} L_{2\ L2j} (OH)_{wj}$

Where $M_1j$, $M_2j$, $L_1j$, and $L_2j$ are positive integers or zero and wj is apositive integer (for a hydrolysed species) zero or negative integer (for protonated species) .The constant calculated is the "Practical" overall formation constant βj given by the expression:

$$\beta j = \frac{[M_{1\,M1j}\, M_{2\,M2j}\, L_{1\,L1j}\, L_{2\,L2j}\, (OH)_{W\,j}]}{[M_1]^{M1j}\,[M_2]^{M2j}\,[L_1]^{L1j}\,[L_2]^{L2j}\,(OH)^{W\,j}}$$

Where square brackets [ ] denote concentration and braces { } denote activities.

The main program deals with input of data the setting up and solution of the least square equation and output of the results. In SCOGS, refinement consists of minimizing the sum of the squares of residuals in titre $\Sigma_1 R_1$ where for $i^{th}$ point $R_1$ (actual titre of base) – (titre calculated from input data using current estimates of the constants and the experimental of pH). The calculation begins with the reading of the input data, formats and other details of which are provided with a listing of the program. The constitution of each species must be given together with an estimate of the constants and the experimental value of pH.

Thus, this program has been used successfully in the refinement of data of ternary and quaternary complexes studied in the present work.

## PROCEDURE

In the present thesis a study has been done on some mixed ligand MAB (ternary) and multimetal–multiligand $M_1M_2AB$ (quaternary) complexes of Cu(II), Ni(II), Co(II), Zn(II) with nucleic acid (Pyrimidine) bases , Uracil , Thymine and some amino acids Lysine , Proline ,Asparagine , Valine .The stability constants are determined at 37± 1°C temperature by potentiometry in aqueous medium . In the present chapter, the experimental methods employed in this study would be briefly described.

## Materials

### Double Distilled Water

Double distilled water was boiled to expel any free carbon dioxide called and collected in well stopped pyrex flask. The pH of this water approx. 6.97.

### Sodium Nitrate(A.R.)

A 1.0 M stock solution of sodium nitrate was prepared and used to maintain the constant ionic strength.

### Nitric Acid (A.R.)

A 0.02 M stock solution of nitric acid was prepare and standardized against a carbonate free sodium hydroxide solution. Which had earlier been standardized against a standard oxalic acid (A.R.) solution.

### Sodium Hydroxide Solution

A 0.1 M carbonate free sodium hydroxide solution was prepared in double distilled water according to the method of Allen and Low (E'). This solution was standardized against a standard oxalic acid (A.R.) solution. Sodium hydroxide solution was used as a titrant.

### Ligand Solution

A 0.01 M solutions of Uracil, Thymine, Lysine, Proline, Valine and Asparagine (Loba chemicals) were prepared separately by weighing the requisite amount and dissolving in double distilled water.

### Metal Ion Solutions

Following metal ion solutions were prepared in the study of complex formation.

1. Cobalt Nitrate (A.R.)
2. Nickel Sulphate (A.R.)
3. Copper Nitrate (A.R.)
4. Zinc Sulphate (A.R.)

Solutions of the above metal ions were prepared and standardized by EDTA titrations (F').

## Instruments Used

### pH meter

pH measurements were done by an electric digital pH meter (century-model CP 901-S) with a glass electrode supplied with the instrument and working on 220V/50 cycles stabilized by A.C.mains. The pH meter has a reproducibility of ±0.01 pH . The electrode of pH meter was conditioned monthly by saturated Potassium chloride (BDH) solution.

### Calibration of pH-meter Scale

Before starting each set of observations, the pH meter was calibrated with buffer solutions of pH (4.0) and pH (9.2) respectively which was prepared by dissolving buffer tablets (BDH) in double distilled water in appropriate concentrations. After completion of whole set, the calibration was again checked with buffer of pH = 4.0 and was found to remain unaltered.

### Titrating Vessel

Titrating vessel was a specially designed double walled beaker of capacity 100 ml, made of pyrex glass. It is fitted with on inlet and outlet for circulation of water to maintain a constant temperature.

**Thermostate**

An ultra thermostate type $U_{10}$ (VEB MLW Sitz, Freital, Germany) was used to maintain a constant temperature in all the experiments.

**Magnetic Stirrer**

A SONAR magnetic stirrer 2 MLH was used for constant stirring of the solution mixtures throught the experiment.

**Conditions of Study**

All the experiments were carried out in an atmosphere of purified nitrogen by bubbling it through the solution in which the electrode was dipping. The nitrogen gas thus serves to prevent atmospheric oxidation and also to stir the solution.

**Magnetic Stirrer**

A SONAR magnetic stirrer 2 MLH was used for constant stirring of the solution mixtures throughout the experiment.

## Titration Procedure

For all, binary, ternary and quaternary systems following solution mixtures were prepared keeping the total volume 50 ml in each case.

**Solution A:** 5 ml $NaNO_3$ (1.0 M) + 5ml $HNO_3$ (0.02M) + water

**Solution B:** 5 ml $NaNO_3$ (1.0 M) + 5ml $HNO_3$ (0.02M) + 5ml A (0.01M) + water

**Solution C:** 5 ml $NaNO_3$ (1.0 M) + 5ml $HNO_3$ (0.02M) + 5ml A (0.01M) + 5 ml $M_1$(II) (0.01M) + water

**Solution D:** 5 ml $NaNO_3$ (1.0 M) + 5ml $HNO_3$ (0.02M) + 5ml A (0.01M) + 5 ml $M_1$(II) (0.01M) + 5ml B (0.01M) + water

**Solution E :** 5 ml $NaNO_3$ (1.0 M) + 5ml $HNO_3$ (0.02M) + 5ml A (0.01M) + 5 ml $M_1$(II) (0.01M) + 5ml B(0.01M) + 5ml $M_2$(II) (0.01M) + water

Where $M_1$ (II) and $M_2$ (II) are Co / Ni / Cu and Zn

A = Primary ligand i.e. Lysine / Valine / Proline / Asparagine

and

B = Secondary ligand i.e. Uracil / Thymine .

Total volume in each case was raised upto 50 ml and ionic strength (I) of all solutions was maintained constant I = 0.1 M.($NaNO_3$).

Each set of solution was then titrated against alkali (NaOH). The pH meter reading with progressive addition of alkali to the titration mixtures were noted, when the reading of pH meter stabilized. The pH values were plotted against the volume of NaOH and the titration curves were obtained. The titration were discontinued of the appearance of turbidity.

# Chapter 4

# *Results & Discussion*

## Ternary Metal Chelates

The results of potentiometric investigation on Lysine-M(II)-Uracil, Proline-M(II)-Uracil, Valine-M(II)-Thymine and Asparagine-M(II)-Thymine system have been presented in aqueous medium at 37±1°C and I=0.1M $NaNO_3$, where M(II)=Co(II)/ Ni(II)/ Cu(II)/Zn(II). In addition to the binary metal chelates, the formation of ternary metal chelates has been favoured as detected by pH titration curves (fig. 4.1-4.16) and species distribution curves (fig. 4.17-4.32)

**Titration curves** - The following solution sets were prepared in aqueous medium, keeping molar ratio 1:1:1 and total volume 50 ml in each case:

***Solution A-*** 5ml $NaNO_3$ (1.0M) + 5ml $HNO_3$ (0.02M) + 40ml $H_2O$

***SolutionB-*** 5ml $NaNO_3$ (1.0M) + 5ml $HNO_3$ (0.02M) + 5ml A (0.01M) + 35ml $H_2O$

***SolutionC-*** 5ml $NaNO_3$ (1.0M) + 5ml $HNO_3$ (0.02M) + 5ml A (0.01M) + 5ml M(II)(0.01M)+ 30ml $H_2O$

***SolutionD-*** 5ml $NaNO_3$ (1.0M) + 5ml $HNO_3$ (0.02M) + 5ml A (0.01M) + 5ml M(II)(0.01)+ 5ml B (0.01M) + 25ml $H_2O$

Overall strength of acid = 0.002 M $HNO_3$

Overall strength of the ligand = 0.001M (A/B)

Overall strength of M (II) = 0.001M

Overall ionic strength I = 0.1M $NaNO_3$

Strength of alkali = 0.1M NaOH

Where,

A= Primary ligand i.e. Lysine/Valine/Proline/Asparagine

B= Secondary ligand i.e. Uracil/Thymine

M (II) = Co/Ni/Cu/Zn

Procedure for the titration has already been described in the chapter III of the thesis.

The plot of pH values against the volume of alkali gives the titration curves A, B, C and D representing acid, ligand, binary and ternary species respectively. Titration curves are shown in fig. (4.1-4.16). The formation of ternary metal chelates in solution is deduced from the fact that the curve 'D' shows a displacement with respect to curve 'C' along the volume axis.

**SPECIES DISTRIBUTION CURVES:**

Species distribution curves are obtained by plotting percent (%) concentration of the species obtained through SCOGS computer technique against pH. The distribution curves are finally sketched by running the computer program ORIGIN 4.0 and are shown in fig. (4.17-4.32).

## Co(II)-Lysine-Uracil (1:1:1) System

Potentiometric titration curves and the Speciation curves [Co(II)-Lysine-Uracil] system are presented in fig.(4.1) and fig.(4.17) respectively. The mixed ligand complex i.e. ternary complex species, protonated ligand species;$AH_3$, $AH_2$, AH, BH and the binary complex species CoB exist in good concentration.

The free metal ion also exist in appreciable concentration. It is clearly evident from the speciation curves that the concentration of $AH_3$, $AH_2$, AH and BH species decreases with increase in pH. All the protonated species of both ligands exist in the pH range ~3.0-9.8. This type of decreasing trend

indicates the formation of complex. The concentration of hydroxo species is found to be very low existing in the pH range ~8.1-10.4.

Speciation curves reveal that [Co(II)-Uracil] binary complex is the major species whose concentration is maximum ≈80% at pH ~8.0. With further increase in pH there is gradual decrease in the concentration of binary complex. On the other hand, the binary complex [Co(II)-Lysine] also exist in the pH range ~7.2-10.5. Its concentration increases with increase in pH maximum up to ≈5% showing its maximum presence ≈ 5% at pH~9.0.

From the distribution profiles, it appears that the binary complexes are formed according to the equilibria:

$$[AH]^{2-} + Co^{2+} \rightleftharpoons [Co(II)\text{-}A]^{-} + H^{+}$$

$$[BH]^{-} + Co^{2+} \rightleftharpoons [Co(II)\text{-}BH]^{+}$$

The concentration profiles of [Co(II)-Lysine-Uracil] indicate the formation of mixed ligand complex in the pH range ~7.4- 10.5. There is a gradual decrease in concentration of binary CoB complex species with a concomitant increase in the concentration of ternary complex species CoAB attaining the maximum concentration of ≈79% at pH ~10.3, which shows the following equilibria:

$$[Co(II)\text{-}BH]^{+} + [AH]^{2-} \rightleftharpoons [Co(II)\text{-}A\text{-}BH]^{2-} + H^{+}$$

$$[Co(II)\text{-}A]^{-} + [BH]^{-} \rightleftharpoons [Co(II)\text{-}A\text{-}BH]^{2-}$$

Very small proportion of metal hydroxo species viz. $Co(II)(OH)^+$ and $Co(II)(OH)_2$ exist in the pH range ~8.0-10.5. The formation of hydroxo species support the of mixed ligand or ternary complex.

$$Co^{2+} + H_2O \rightleftharpoons Co(II)(OH)^+ + H^+$$

$$Co^{2+} + 2H_2O \rightleftharpoons Co(II)(OH)_2 + 2H^+$$

## Ni(II)-Lysine-Uracil (1:1:1) System

pH titration curves and Formation curves for [Ni(II)-Lysine-Uracil] system are presented in fig.(4.2) and fig.(4.18) respectively. The ternary complex species, shows its remarkable presence at higher pH range. Protonated ligand species; $AH_3$, $AH_2$, AH, BH and the binary complex species NiA and NiB exist in appreciable amount. The free metal ion is found to follow a declining pattern and hydroxo species of $Ni^{2+}$(aq.) metal ion is identifiable in low concentration at pH>8.0.

Formation of complex species may be attributed to the fall in the protonated ligand as well as $Ni^{2+}$(aq.) metal ion.It is clear from the Speciation diagram that the [Ni(II)-Uracil] binary complex is the major complex species whose concentration is ≈75% at pH ~7.5 . With further increase in pH its concentration gradually decreases. On the other hand, the species [Ni(II)-Lysine] exists in the pH range ~6.4-10.5 and its gradually increases with increase in pH attaining a maximum up to ≈32% at pH ~ 8.5.

From the distribution profiles, it appears that the binary complexes are formed according to the equilibria:

$$[AH_2]^- + Ni^{2+} \rightleftharpoons [Ni(II)\text{-}A]^- + 2H^+$$

$$[BH]^- + Ni^{2+} \rightleftharpoons [Ni(II)\text{-}BH]^+$$

The concentration profiles of [Ni(II)-Lysine-Uracil] indicate the formation of mixed ligand complex in the pH range ~7.3-10.5. There is a gradual increase in the concentration of NiAB complex species attaining the maximum concentration ≈72% at pH ~10.5, which shows the following equilibrium to occur:

$$[Ni(II)\text{-}A]^- + [BH]^- \rightleftharpoons [Ni(II)\text{-}A\text{-}BH]^{2-}$$

$$[Ni(II)\text{-}BH]^+ + [AH]^{2-} \rightleftharpoons [Ni(II)\text{-}A\text{-}BH]^{2-} + H^+$$

The binary complexation equilibrium has been found to be overlapping with the hydrolytic equilibrium of metal ion according to the following equation:

$$Ni^{2+} + 2H_2O \rightleftharpoons Ni(II)(OH)_2 + 2H^+$$

$$[Ni(II)A]^- + 2H_2O \rightleftharpoons Ni(II)(OH)_2 + [H_2A]^-$$

## Cu(II)-Lysine-Uracil ( 1:1:1) System

Titration curves and Species distribution curves for [Cu (II)-Lysine-Uracil] system are presented in fig.(4.3) and fig.(4.19) respectively. The ternary complex species, protonated ligand species $AH_3$, $AH_2$, AH, BH and the binary complex species CuA and CuB exist in good concentration. The free metal ion and metal hydroxo species do not exist throughout the entire pH range.

It is clearly evident from the Speciation curves that the concentration of $AH_3$, $AH_2$, AH and BH species of both the ligands are found to be decreasing within the pH range ~3.0-5.0 indicating the metal ligand complexation. The concentration of free $Cu^{2+}$ aqueous ion does not exist which indicates its involvement in the complex formation.

Speciation curve reveals that [Cu(II)-Lysine], [Cu(II)-Uracil] binary complexes are the major species whose concentration are ≈ 65% and ≈62% at pH ~5.5 and ~5.0 respectively. With further increase in pH their concentrations gradually decrease, which is probably due to the formation of hydroxo species. Binary complex is formed according to the equilibrium:

$$[AH_2]^- + Cu^{2+} \rightleftharpoons [Cu(II)\text{-}A]^- + 2H^+$$

$$[BH]^- + Cu^{2+} \rightleftharpoons [Cu(II)\text{-}BH]^+$$

The concentration profiles of [Cu(II)- Lysine-Uracil] indicate the formation of mixed ligand complex in the pH range ~3.5-9.0.The concentration of mixed ligand CuAB complex species increases with concomitant decrease of binary complex, CuB, CuA species and attains a concentration of ≈55% at pH ~ 8.5, which shows the formation of complex. Complexation equilibria has been derived on the basis of the speciation curves of the complex occurring at different pH.

$$[Cu(II)\text{-}BH]^+ + [AH_2]^- \rightleftharpoons [Cu(II)\text{-}A\text{-}BH]^{2-} + 2H^+$$

$$[Cu(II)\text{-}A]^- + [BH]^- \rightleftharpoons [Cu(II)\text{-}A\text{-}BH]^{2-}$$

The simultaneous formation of ternary complex may be expressed as per equilibrium:

$$[AH_2]^- + Cu^{2+} + [BH]^- \rightleftharpoons [Cu(II)\text{-}A\text{-}BH]^{2-} + 2H^+$$

## Zn(II)-Lysine-Uracil (1:1:1) System

Fig.(4.4) and fig.(4.20) represent the Titration curves and Species distribution curves for [Zn(II)-Lysine-Uracil] system respectively. Speciation curves reveal the existence of following species; protonated ligand species, free metal ion, binary and ternary complex species in the variable concentration profile.

The speciation curves clearly shows that the concentration of $AH_3$, $AH_2$, AH and BH species of both the ligand are decreasing with increase in pH range ~3.1-8.0.

The free metal Zn(II) is found in sufficient amount, at the start and following a decline pattern indicating the formation of mixed ligand complex.

The species present in maximum abundance is the binary complex [Zn(II)-Uracil] whose concentration is maximum ≈75% at pH ~7.5 . With further increase in pH its concentration gradually decreases, which is probably due to the formation of ternary complex ZnAB. On the other hand, the binary complex [Zn(II)-Lysine] exist in the pH range ~6.9-10.0, and its concentration gradually increases with increase at higher pH maximum up ≈25% .

From the distribution profiles, it appears that the binary complexes are formed according to the equilibria:

$$[AH]^{2-} + Zn^{2+} \rightleftharpoons [Zn(II)\text{-}A]^- + H^+$$

$$[BH]^- + Zn^{2+} \rightleftharpoons [Zn(II)\text{-}BH]^+$$

The mixed ligand complex [Zn(II)-Lysine] exist in the pH range ~7.4-10.0 . There is a gradual increase in concentration of ZnAB complex species attaining the maximum concentration of ≈45% at pH ~9.2 with decrease in binary complex ZnB species in the same pH range. Speciation curves suggest the formation of the ternary complex according to following equilibrium:

$$[Zn(II)\text{-}BH]^+ + [AH]^{2-} \rightleftharpoons [Zn(II)\text{-}A\text{-}BH]^{2-} + H^+$$

$$[Zn(II)\text{-}A]^- + [BH]^- \rightleftharpoons [Zn(II)\text{-}A\text{-}BH]^{2-}$$

Formation of hydroxo species $Zn(II)(OH)^+$ have been taken into consideration. The proportion of hydroxo species are found to be remarkable at higher pH range ~8.2- 9.4. Hydroxo species indicates the dissociation of metal chelates, involving following equilibrium:

$$Zn^{2+} + H_2O \rightleftharpoons Zn(II)(OH)^+ + H^+$$

## Co(II)-Proline-Uracil ( 1:1:1) System

Titration curves and Formation curves for [Co(II)-Proline-Uracil] system are presented in fig.(4.5) and fig.(4.21) respectively. Mixed ligand complexation equilibrium involves ternary complex species; $AH_2$, AH, BH and binary ZnA exist in good concentration and binary complex species CoA present in genuine concentration.

The buffer region ~3.0-5.5 corresponding to deprotonation of ligand is lowered in the presence of $Co^{2+}$ aqueous ions. It is clearly indicated that the

concentration of $AH_2$ and BH species decreases with increase in pH while the concentration of AH species primarily increase and then decrease with incline in pH. This type of trend in the above species indicates the complexation.

Speciation curves reveal that [Co(II)-Proline] binary complex species is found to show its predominance in the lower pH region ~3.0-5.0, attaining the maximum value ≈29% at pH ~4.5. Complexation starts in the beginning with the addition of alkali. With further increase in pH, there is gradual decrease in the concentration of [Co(II)-Proline] binary complex. On the other hand, [Co(II)-Uracil] does not exist throughout the entire pH range. The equilibrium involved in the binary complex formation of the type [Co(II)-A] can be represented by the following equation:

$$[AH_2] + Co^{2+} \rightleftharpoons [Co(II)\text{-}A] + 2H^+$$

$$[AH]^- + Co^{2+} \rightleftharpoons [Co(II)\text{-}A] + H^+$$

It is observed from the distribution diagram that the [Co(II)-A-B] species predominate in the entire pH range ~7.5-11.0, which confirms the formation of complex. There is gradual decrease in the concentration of binary complex CoA, while the ternary species shows maximum presence at pH ~10 (≈59%) in the system. Its concentration then decrease gradually up to pH ~11.0 due to the formation of hydroxo species. The formation of ternary complexes governed according to the equilibrium given below:

$$[Co(II)\text{-}A] + [BH]^- \rightleftharpoons [Co(II)\text{-}A\text{-}BH]^-$$

The another equilibrium of ternary metal chelates may be assumed to take place as:

$$[AH]^- + Co^{2+} + [BH]^- \rightleftharpoons [Co(II)\text{-}A\text{-}BH]^- + H^+$$

The metal hydroxo species i.e. $Co(II)(OH)^+$ and $Co(II)(OH)_2$ are formed at higher pH ~8.5-11.0, which indicates the complexation of mixed chelates. The formation equilibria can be written as:

$$Co^{2+} + H_2O \rightleftharpoons Co(II)(OH)^+ + H^+$$

$$Co^{2+} + 2H_2O \rightleftharpoons Co(II)(OH)_2 + 2H^+$$

## Ni(II)-Proline-Uracil -( 1:1:1) System

Titration curves for [Ni(II)-Proline- Uracil] system are presented in fig. (4.6) and Speciation curves in fig.(4.22) which clearly indicate that maximum complex formation occurs at pH ~8.5. The ternary complex species, protonated ligand species; $AH_2$, AH, BH, binary complex species NiA and NiB exists in adequate concentration. The free metal ions and hydroxo species are also present in the lower and higher pH region respectively.

It is clearly evident from the speciation curves that the concentration of $AH_2$ and BH species of both the ligands are found to be decreasing with increase in pH whereas that of species AH increasing within the pH range ~3.0- 4.0, while decreasing with in pH range ~4.0-10.5. The free metal ion $Ni^{2+}$(aq.) gradually decreases with increase in pH, which indicate, its involvement in the complex formation.

It is clear from distribution curves that binary species [Ni(II)-Proline] is found to be $\approx$75%, its predominance being at the pH ~7.5. On the other

hand, the species [Ni(II)-Uracil] is evident in the pH region ~4.1-10.5 and its concentration gradually increases with increase in pH attaining maximum up ≈ 16%. At higher pH region, there is gradual decline in the concentration of [Ni(II)-Proline] and [Ni(II)-Uracil] species due to the appearance of hydroxo species.

From the distribution profile, it appears that the binary complexes are formed according to the equilibria:

$$[AH_2] + Ni^{2+} \rightleftharpoons [Ni(II)\text{-}A] + 2H^+$$

$$[AH]^- + Ni^{2+} \rightleftharpoons [Ni(II)\text{-}A] + H^+$$

$$[BH]^- + Ni^{2+} \rightleftharpoons [Ni(II)\text{-}BH]^+$$

There is gradual increase in the concentration of NiAB species. Its concentration increases with concomitant decrease of binary complex [Ni(II)-A] and [Ni(II)-B] respectively and attains maximum concentration ≈77% at pH ~10.2. Complex formation in aqueous solution may be described according to the following equilibrium:

$$[Ni(II)\text{-}A] + [BH]^- \rightleftharpoons [Ni(II)\text{-}A\text{-}BH]^-$$

$$[Ni(II)\text{-}BH]^+ + [AH]^- \rightleftharpoons [Ni(II)\text{-}A\text{-}BH]^- + H^+$$

Complexation equilibrium may be assumed to take place in another form as:

$$[AH]^- + Ni^{2+} + [BH]^- \rightleftharpoons [Ni(II)\text{-}A\text{-}BH]^- + H^+$$

The hydroxo species $Ni(II)(OH)^+$ is identified in the pH range ~8.2-10.5 involving the following equilibrium:

$$Ni^{2+} + H_2O \rightleftharpoons Ni(II)(OH)^+ + H^+$$

## Cu(II)-Proline-Uracil (1:1:1) System

Titration curves and Species distribution diagram of the present system are shown in fig.(4.7) and fig.(4.23) respectively. Speciation curves clearly indicate the existence of protonated ligand species in the decreasing order of their concentration $AH_2$ and AH species of the ligand Proline show their maximum presence at pH ~3.2, their concentration at this pH being ≈70% and ≈37% respectively. With the rise in pH their concentrations are found to follow a declining pattern. Similarly, the maximum concentration of the protonated species of the secondary ligand i.e. BH shows its maximum existence at pH ~3.2 (≈100%). Following the same pattern, fall in the concentration is accompanied with the increase in pH. It may be concluded that both the ligands undergo the process of complexation with Cu metal ion, which is also present in decreasing order.

The formation of binary complex may be assumed to follow the equilibrium:

$$[AH_2] + Cu^{2+} \rightleftharpoons [Cu(II)\text{-}A] + 2H^+$$

$$[AH]^- + Cu^{2+} \rightleftharpoons [Cu(II)\text{-}A] + H^+$$

The concentration of [Cu(II)-Proline] complex increases gradually attaining a maximum value at pH~5.0 (≈40 %), thereafter there is a gradual decline in its concentration up to negligible amount of pH ~9.0. Now after the addition of secondary ligand an appreciable amount of ternary complex has been found to present in increasing order of its concentration.

The stepwise formation of mixed ligand complex may be explained as per equilibrium:

$$[Cu(II)\text{-}A] + [BH]^{-} \rightleftharpoons [Cu(II)\text{-}A\text{-}BH]^{-}$$

Its simultaneous formation may be assume to take place as:

$$[AH]^{-} + Cu^{2+} + [BH]^{-} \rightleftharpoons [Cu(II)\text{-}A\text{-}BH]^{-} + H^{+}$$

Formation curves clearly indicate that the gradual incline in the concentration of ternary complex continues up to pH ~7.0 with a maximum abundance of approximately ≈ 90%. Concomitant decline in binary complex species shows formation of mixed chelates.

Formation of hydroxo species has been taken into consideration as ternary complexation equilibrium has been found to be overlapping the hydrolytic equilibrium of $Cu^{2+}$(aq.) ion as per equilibrium.

$$Cu^{2+} + 2H_2O \rightleftharpoons Cu(II)(OH)_2 + 2H^{+}$$



## Zn(II)-Proline-Uracil ( 1:1:1) System

Titration curves for [Zn(II)-Proline-Uracil] system are presented in fig.(4.8) and Speciation curves in fig.(4.24). By pH titration data, it is clearly evident that the releasing of proton is within the pH range ~3.0-8.0. The present investigation indicates complex formation with the metal ion. The curve D set apart from curve C at the pH ~8.2. Protonated ligand species; viz. $AH_2$, AH, BH, binary complex species [Zn(II)-Proline], [Zn(II)-Uracil] and ternary complex species [Zn(II)-Proline-Uracil] are existant species in the present system. The free metal ion and metal hydroxo species also present in the system.

The formation curves clearly shows that the concentration of $AH_2$ and BH of the both ligands are found to be decreasing from ≈9% and ≈33%

with increase in pH whereas the AH is increasing in the pH range ~3.0-4.2, AH attains maximum concentration ≈85%, while decreasing in the pH range ~4.2-8.4, indicating the metal ligand complex formation. The free metal ion in the system gradually decreases with increase in pH, which indicates its coordination with the ligand.

The binary complex [Zn(II)-Proline] is the major species whose concentration is maximum ≈65% at pH~8.2. With further increase in pH its concentration gradually decreases which is probably due to the formation of ternary complex ZnAB. On the other hand, [Zn(II)-Uracil] does not exist in the entire pH range.

From the distribution profile, it appears that the binary complexes are found according to the following profile:

$$[AH_2] + Zn^{2+} \rightleftharpoons [Zn(II)\text{-}A] + 2H^+$$

$$[AH] + Zn^{2+} \rightleftharpoons [Zn(II)\text{-}A] + H^+$$

The concentration profile of [Zn(II)-Proline-Uracil] indicates the formation of mixed ligand complex in the pH range ~7.9-9.1. It is clear that the concentration of ZnAB complex species attains the maximum concentration ≈35% at pH ~9.1 with the binary complex ZnA species in the pH range ~8.0-9.1. The stepwise formation of mixed ligand complex may be explained as per equilibrium:

$$[Zn(II)\text{-}A] + [BH]^- \rightleftharpoons [Zn(II)\text{-}A\text{-}BH]^-$$

Its simultaneous formation may be assumed to take place as:

$$[AH]^- + Zn^{2+} + [BH]^- \rightleftharpoons [Zn(II)\text{-}A\text{-}BH]^- + H^+$$

The formation of hydroxo complexes were also considered in calculating the metal ligand constants. The hydroxo species formed in the pH range ~3.0-4.3, and declined at higher pH region shows the formation of binary and ternary complexes at higher pH region.

$$Zn^{2+} + H_2O \rightleftharpoons Zn(II)(OH)^{+} + H^{+}$$

## Co(II)-Valine -Thymine (1:1:1) System

pH titration curves and Speciation curves for [Co(II)-Valine-Thymine] system are presented in fig.(4.9) and (4.25) respectively. The mixed ligand species $AH_2$, AH, BH, binary free metal ion and hydroxo species exist throughout the entire pH range.

The concentration of $AH_2$, AH and BH species of both ligands are found in the complex formation. The complexation equilibria of binary species:

$$[BH]^{-} + Co^{2+} \rightleftharpoons [Co(II)\text{-}BH]^{+} + H^{+}$$

It is clear from the Species distribution curves that binary complex [Co(II)-Thymine] is the major species whose concentration is ≈31% and pH ~7.5, with further increase in pH its concentration gradually decreases, which is probably due to the formation of ternary complex [Co(II)-A-BH]. On the other hand, the species [Co(II)-Valine] does not exist in the system. The free metal ion Co(II) is found in declining pattern, which indicates its involvement in the complex formation.

Formation curves clearly indicates the formation of mixed ligand complex in the pH range ~7.3-10.5. The incline in the concentration of [Co(II)-A-BH] complex species attains the maximum concentration ≈87%

at pH ~9.5, with decrease in binary complex [Co(II)-BH] species. The formation of ternary complex according to following equilibria:

$$[AH]^- + Co^{2+} + [BH]^- \rightleftharpoons [Co(II)\text{-}A\text{-}BH]^- + H^+$$

$$[Co(II)\text{-}BH]^+ + [AH]^- \rightleftharpoons [Co(II)\text{-}A\text{-}BH]^- + H^+$$

The metal hydroxo species viz. $Co(II)(OH)^+$ and $Co(II)(OH)_2$ exist in the pH range ~7.4-10.5 involving the following equilibrium :

$$Co^{2+} + H_2O \rightleftharpoons Co(II)(OH)^+ + H^+$$

$$Co^{2+} + 2H_2O \rightleftharpoons Co(II)(OH)_2 + 2H^+$$

## Ni(II)-Valine-Thymine (1:1:1) System

Fig.(4.10) represents the Titration curves of the present system and Species distribution curve are shown in fig.(4.26). Protonated ligand species; $AH_2$, AH, BH and binary complex species NiA exist in genuine concentration, while NiB present in small proportion. The free metal ion and hydroxo species also exist in the system.

The formation curve clearly indicates that concentration of $AH_2$, AH and BH species of both ligands are found to be decreasing with increase in pH, whereas concentration of species AH decreasing with increase in the pH range ~3.5-9.5, indicating the metal-ligand complexation.

The declining pattern of free ion $Ni^{2+}$(aq.) with increase in pH, indicates its involvement in the complex formation.

It is clear from the speciation curves that [Ni(II)-Valine] binary complex is the major species whose concentration is $\approx$79% and pH ~7.0, with further increase in pH its concentration gradually decreases. On the other hand, the species [Ni(II)-Thymine] also exist in the higher pH range ~6.4-9.4.

From the distribution profiles, it appears that the binary complexes are formed according to following equilibrium:

$$Ni^{2+} + [AH]^{-} \rightleftharpoons [Ni\ (II)\text{-}A] + H^{+}$$

$$Ni^{2+} + [BH]^{-} \rightleftharpoons [Ni(II)\text{-}BH]^{+} + H^{+}$$

The appearance of mixed ligand complex [Ni(II)-Valine-Thymine] in the pH range ~6.4-10.3. There is a gradual increase in the concentration of NiAB complex species attaining the maximum concentration ≈75% at pH ~9.5. The decrease in the binary complex NiA and NiB shows the following equilibrium:

$$[AH]^{-} + Ni^{2+} + [BH]^{-} \rightleftharpoons [Ni(II)\text{-}A\text{-}BH]^{-} + H^{+}$$

$$[Ni(II)\text{-}A] + [BH]^{-} \rightleftharpoons [Ni(II)\text{-}A\text{-}BH]^{-}$$

$$[Ni(II)\text{-}BH]^{+} + [AH]^{-} \rightleftharpoons [Ni(II)\text{-}A\text{-}BH]^{-} + H^{+}$$

The hydroxo species $Ni(II)(OH)_2$ is identified in the pH range ~8.0-10.4 and attains maximum concentration ≈25%, involving the following equilibrium:

$$Ni^{2+} + 2H_2O \rightleftharpoons Ni(II)(OH)_2 + 2H^{+}$$

## Cu(II)-Valine-Thymine (1:1:1) System

Mixed ligand complex species is the major species making its ≈87% contribution, as is evidenced from the Species distribution curve of the present system fig.(4.27). Ternary complexation starts from pH ~4.0 and after a gradual increase in the concentration of CuAB complex, its concentration attaining a maximum value ≈87% at pH ~9.0.

The rise in concentration of ternary complex species is favoured due to decline in the concentration of protonated ligand species and of $Cu^{2+}$(aq.) metal ions as well.

Following equilibrium may be assumed to occur:

$$[AH]^- + Cu^{2+} + [BH]^- \rightleftharpoons [Cu(II)\text{-}A\text{-}BH]^- + H^+$$

$$[Cu(II)\text{-}BH]^+ + [AH]^- \rightleftharpoons [Cu(II)\text{-}A\text{-}BH]^- + H^+$$

$$[BH]^- + [Cu(II)\text{-}A] \rightleftharpoons [Cu(II)\text{-}A\text{-}BH]^-$$

Two types of binary complex species have been found to present according to the formation equilibrium:

$$[AH_2] + Cu^{2+} \rightleftharpoons [Cu(II)\text{-}A] + 2H^+$$

$$[AH]^- + Cu^{2+} \rightleftharpoons [Cu(II)\text{-}A] + H^+$$

$$[BH]^- + Cu^{2+} \rightleftharpoons [Cu(II)\text{-}BH]^+$$

Now decline in the concentration of binary complex species with the concomitant incline in the concentration of ternary complex may be explained as per equilibrium:

$$[Cu(II)\text{-}A] + [BH]^- \rightleftharpoons [Cu(II)\text{-}A\text{-}BH]^-$$

After pH ~9.0, a gradual decline in concentration of complex species is observed, which is probably due to the formation of hydroxo species:

$$Cu^{2+} + 2H_2O \rightleftharpoons Cu(II)(OH)_2 + 2H^+$$

Thus, metal-ligand formation equilibrium has been found to be overlapping with the hydrolytic equilibrium of $Cu^{2+}$(aq.) metal ions.

## Zn(II)-Valine-Thymine (1:1:1) System

Titration and Formation curves for [Zn(II)-Valine-Thymine] system are presented in fig.(4.12) and fig.(4.28) respectively. The protonated ligand species; $AH_2$, AH, BH and binary complex species ZnA exist in good concentration. The free metal ion and hydroxo species also exist throughout the entire pH range.

Mixed ligand complex species is the predominant species making its ≈75% contribution, as is evidenced from the speciation curves of the present system. Ternary complexation starts at higher pH ~7.0 and after a gradual increase in the concentration of [Zn(II)-Valine-Thymine] complex. The rise in concentration of ternary complex species is favoured due to decline in concentration of protonated ligand species $AH_2$, AH and BH. The metal hydroxo species also involved in the complex formation at higher pH. The concentration of free metal ion $Zn^{2+}$(aq.) decreases with the pH, which indicates its involvement in the complex formation according to the following equilibrium:

$$[AH]^- + Zn^{2+} + [BH]^- \rightleftharpoons [Zn(II)\text{-}A\text{-}BH]^- + H^+$$

$$[Zn(II)\text{-}BH]^+ + [AH]^- \rightleftharpoons [Zn(II)\text{-}A\text{-}BH]^- + H^+$$

Two types of binary complex species have been found to present according to the formation equilibria:

$$[BH]^- + Zn^{2+} \rightleftharpoons [Zn(II)\text{-}BH]^+$$

Speciation curves reveals that the [Zn(II)-Thymine] binary complex species is the major species whose concentration is maximum ≈50% at pH

~7.0, with further increase in pH its concentration gradually decreases. On the other hand, the species [Zn(II)-Valine] does not exist in the system.

The protonation of the metal hydroxo species $M(II)(OH)^+$ are $M(II)(OH)_2$ found to be in higher pH region, which shows the following equilibrium:

$$Zn^{2+} + 2H_2O \rightleftharpoons Zn(II)(OH)_2 + 2H^+$$

## Co(II)-Asparagine-Thymine (1:1:1) System

Titration curves for [Co(II)-Asparagine-Thymine] are presented in fig.(4.13) and Formation curves are represented in fig.(4.29). The protonated ligand species i.e. $AH_2$, AH, BH, binary CoA and CoB exist in good concentration. The free metal ion and hydroxo species also exist in the system.

All the protonated species $AH_2$, AH and BH species decrease with increase in pH in the range ~3.0-10.0. This type of trend in the concentration profile indicates the formation of complex. The speciation curve clearly reveals that [Co(II)-Asparagine] binary complex is the major species whose concentration is maximum ≈25% at pH ~7.0. With further increase in pH there is a gradual decrease in the concentration of binary complex. On the other hand, [Co(II)-Thymine] also exists in the pH range ~6.5-9.7.

From the distribution profiles it appears that the binary complexes are formed according to equilibria:

$$[AH]^- + Co^{2+} \rightleftharpoons [Co(II)\text{-}A] + H^+$$

$$[BH]^- + Co^{2+} \rightleftharpoons [Co(II)\text{-}BH]^+$$

The gradual decline in the concentration of binary complexes [Co(II)-A] and $[Co(II)-BH]^+$, the concomitant incline in concentration of ternary complex species $[Co(II)-A-BH]^-$ attaining a maximum concentration of ≈86% at pH ~9.6 shows the stepwise formation of ternary complex according to the following equilibria:

$$[Co(II)-A] + [BH]^- \rightleftharpoons [Co(II)-A-BH]^-$$

$$[Co(II)-BH]^+ + [AH]^- \rightleftharpoons [Co(II)-A-BH]^- + H^+$$

The alternative simultaneous formation of the complex may be written as:

$$[AH]^- + Co^{2+} + [BH]^- \rightleftharpoons [Co(II)-A-BH]^- + H^+$$

Small proportion of metal hydroxo species viz. $Co(II)(OH)_2$ exist in the pH range ~8.3-10.4 involving the following equilibrium:

$$Co^{2+} + 2H_2O \rightleftharpoons Co(II)(OH)_2 + 2H^+$$

## Ni(II)-Asparagine-Thymine (1:1:1) System

Titration curves for [Ni(II)-Asparagine-Thymine] system are presented in fig.(4.14) and Species distribution curve are represented in fig.(4.30). The protonated ligand species; $AH_2$, AH, BH, binary and ternary complex species exist in good concentration.

It is clearly evident from the speciation curve that all the protonated ligand species $AH_2$, AH and BH exist in declining pattern in the system. The

concentration of free metal ion also decreases with increase in pH, which indicate its involvement in the complex formation.

The two major binary complex species exist in the mixed ligand system. The complexation starts at low pH region and attain maximum value ≈52% and ≈40% respectively. Further increase in the pH, the concentration of binary species decreases which shows the formation of ternary complex. All the binary species exist in the pH range ~3.0-10.3. From distribution profile, it appears that the binary complexes are formed according to the equilibrium:

$$[AH]^- + Ni^{2+} \rightleftharpoons [Ni(II)\text{-}A] + H^+$$

$$[BH]^- + Ni^{2+} \rightleftharpoons [Ni(II)\text{-}BH]^+$$

The mixed ligand complex formation equilibria may be written as follows:

$$[AH]^- + Ni^{2+} + [BH]^- \rightleftharpoons [Ni(II)\text{-}A\text{-}BH]^- + H^+$$

The another equilibria is indicated as follows:

$$[Ni(II)\text{-}BH]^+ + [AH]^- \rightleftharpoons [Ni(II)\text{-}A\text{-}BH]^- + H^+$$

$$[Ni(II)\text{-}A] + [BH]^- \rightleftharpoons [Ni(II)\text{-}A\text{-}BH]^-$$

The concentration of mixed ligand $[Ni(II)\text{-}A\text{-}BH]^-$ complex species incline with concomitant decline of binary complex $[Ni(II)\text{-}BH]^+$ and [Ni(II)-A] species and attains the maximum concentration ≈80% at pH ~10.0.

The metal hydroxo species exist in very low concentration in the ternary system, according to following equilibria:

$$Ni^{2+} + 2H_2O \rightleftharpoons Ni(II)(OH)_2 + 2H^+$$

## Cu(II)-Asparagine-Thymine (1:1:1) System

Formation curve for [Cu(II)-Asparagine-Thymine] system are presented in fig.(4.31). Following species are assumed in ternary system, $AH_2$, AH, BH, $Cu(II)(OH)_2$, binary i.e.[Cu(II)-Asparagine] and [Cu(II)-Thymine], ternary [Cu(II)-Asparagine-Thymine].

Dissociation of ligands starts at same pH ~3.0. The concentration of protonated ligand gradually decrease in the pH range ~3.0-6.4. The free metal ions and hydroxo species are also present in the system. The complexation of binary complexes as follows:

$$[AH]^- + Cu^{2+} \rightleftharpoons [Cu(II)\text{-}A] + H^+$$

$$[BH]^- + Cu^{2+} \rightleftharpoons [Cu(II)\text{-}BH]^+$$

The species distribution curves clearly reveals that the [Cu(II)-Thymine] is major binary species and attain maximum value at pH ~5.5. The [Cu(II)-Asparagine] also exist in the system in the pH range ~3.0-8.5. Further the concentration of binary complexes decreases which indicates the formation of mixed ligand complexes. From distribution profiles, it appears that ternary complex is formed according to the equilibria:

$$[AH]^- + Cu^{2+} + [BH]^- \rightleftharpoons [Cu(II)\text{-}A\text{-}BH]^- + H^+$$

The alternative form of equilibria are indicated as follows:

$$[Cu(II)\text{-}BH]^{+} + [AH]^{-} \rightleftharpoons [Cu(II)\text{-}A\text{-}BH]^{-}$$

The ternary complex species is the predominant species. The concentration of ternary complexes gradually increases with increase in pH and attaining a maximum value ≈82%, further decrease in concentration due to formation of hydroxo species. The hydroxo species also exist in the mixed ligand system. In sufficient proportion of metal hydroxo species viz. $Cu(II)(OH)_2$ exist in the pH range ~6.4-10.0 involving the following equilibria:

$$Cu^{2+} + 2H_2O \rightleftharpoons Cu(II)(OH)_2 + 2H^{+}$$

## Zn(II)-Asparagine-Thymine (1:1:1) System

Following species have been assumed in mixed ligand complexes system as shown in fig.(4.32). The protonated ligand species i.e. $AH_2$, AH, BH, $Zn(OH)_2$, [Zn(II)-Asparagine] and [Zn(II)-Asparagine-Thymine]. The free metal ion is also existing in the system.

The species distribution curves clearly indicate that protonated ligand species and free metal ions are following declining pattern of their concentration with increase in pH.

[Zn(II)-Asparagine] is formed as binary complex species. The binary complexation starts from very beginning of the titration. The concentration of binary complex species is maximum ≈46% at pH ~6.5 whereas [Zn(II)-Thymine] binary complex species is absent in the system. The complex formation equilibrium of binary complex is as follows:

$$[AH]^- + Zn^{2+} \rightleftharpoons [Zn(II)\text{-}A] + H^+$$

The mixed ligand complex is formed somewhat at higher pH region. The concentration of ternary complex species $[Zn(II)\text{-}A\text{-}BH]^-$ increases with concomitant decrease of binary complex [Zn(II)-A] species showing stepwise formation of the complex and attains the maximum concentration ≈ 80% at pH ~9.0. The formation of complex may be explained according to the following equilibria:

$$[AH]^- + Zn^{2+} + [BH]^- \rightleftharpoons [Zn(II)\text{-}A\text{-}BH]^- + H^+$$

The alternative form of equilibrium:

$$[Zn(II)\text{-}A] + [BH]^- \rightleftharpoons [Zn(II)\text{-}A\text{-}BH]^-$$

The hydroxo species $Zn(II)(OH)_2$ is identified in sufficient amount in the pH range ~8.9-10.0, involving the following equilibrium:

$$Zn^{2+} + 2\,H_2O \rightleftharpoons Zn(OH)_2 + 2H^+$$

**Table – 4.1**
**Co(II) - Lysine - Uracil - System**

| Volume of NaOH | pH | | | |
|---|---|---|---|---|
| | A | B | C | D |
| 0.0 | 2.94 | 2.74 | 2.74 | 2.97 |
| 0.2 | 3.00 | 2.84 | 2.83 | 3.20 |
| 0.4 | 3.27 | 2.97 | 2.97 | 3.73 |
| 0.6 | 4.07 | 3.15 | 3.15 | 4.38 |
| 0.8 | 10.14 | 3.4 | 3.49 | 7.35 |
| 1.0 | 10.54 | 6.77 | 6.29 | 8.08 |
| 1.2 | 10.85 | 8.84 | 8.03 | 8.45 |
| 1.4 | 10.99 | 9.40 | 8.57 | 8.62 |
| 1.6 | 11.03 | 9.87 | 9.03 | 8.75 |
| 1.8 | 11.08 | 10.23 | 9.26 | 8.91 |
| 2.0 | 11.15 | 10.47 | 9.5 | 9.1 |
| 2.2 | 11.20 | 10.64 | 9.83 | 9.33 |
| 2.4 | 11.24 | 10.78 | 10.20 | 9.58 |
| 2.6 | 11.28 | 10.89 | 10.41 | 9.58 |
| 2.8 | | 10.97 | 10.56 | 9.85 |
| 3.0 | | 11.05 | 10.69 | 10.10 |
| 3.2 | | 11.11 | 10.73 | 10.16 |

**Table 4.2**
**Ni(II) - Lysine - Uracil - System**

| Volume of NaOH | pH | | | |
|---|---|---|---|---|
| | A | B | C | D |
| 0.0 | 2.94 | 2.74 | 2.72 | 2.73 |
| 0.2 | 3.00 | 2.84 | 2.82 | 2.99 |
| 0.4 | 3.27 | 2.97 | 2.95 | 3.19 |
| 0.6 | 4.07 | 3.15 | 3.51 | 3.67 |
| 0.8 | 10.14 | 3.4 | 6.05 | 6.41 |
| 1.0 | 10.54 | 6.77 | 7.26 | 7.34 |
| 1.2 | 10.85 | 8.84 | 8.09 | 8.03 |
| 1.4 | 10.99 | 9.40 | 9.09 | 8.65 |
| 1.6 | 11.03 | 9.87 | 9.27 | 8.92 |
| 1.8 | 11.08 | 10.23 | 9.59 | 9.10 |
| 2.0 | 11.15 | 10.47 | 9.93 | 9.39 |
| 2.2 | 11.20 | 10.64 | 10.20 | 9.60 |
| 2.4 | 11.24 | 10.78 | 10.41 | 9.83 |
| 2.6 | 11.28 | 10.89 | 10.56 | 10.05 |
| 2.8 | | 10.97 | 10.65 | 10.25 |
| 3.0 | | 11.05 | 10.80 | 10.41 |
| 3.2 | | 11.11 | 10.85 | 10.45 |

**Table 4.3**
**Cu(II) - Lysine - Uracil - System**

| Volume of NaOH | pH | | | |
|---|---|---|---|---|
| | A | B | C | D |
| 0.0 | 2.94 | 2.74 | 2.73 | 2.72 |
| 0.2 | 3.00 | 2.84 | 2.83 | 2.98 |
| 0.4 | 3.27 | 2.97 | 2.97 | 3.17 |
| 0.6 | 4.07 | 3.15 | 3.14 | 3.52 |
| 0.8 | 10.14 | 3.4 | 3.42 | 4.17 |
| 1.0 | 10.54 | 6.77 | 5.80 | 5.03 |
| 1.2 | 10.85 | 8.84 | 6.14 | 6.35 |
| 1.4 | 10.99 | 9.40 | 7.70 | 7.26 |
| 1.6 | 11.03 | 9.87 | 9.51 | 8.16 |
| 1.8 | 11.08 | 10.23 | 10.01 | 8.89 |
| 2.0 | 11.15 | 10.47 | 10.30 | 9.31 |
| 2.2 | 11.20 | 10.64 | 10.51 | 9.65 |
| 2.4 | 11.24 | 10.78 | 10.62 | 9.94 |
| 2.6 | 11.28 | 10.89 | 10.69 | 10.18 |
| 2.8 | | 10.97 | 10.73 | 10.38 |
| 3.0 | | 11.05 | 10.77 | 10.54 |
| 3.2 | | 11.11 | 10.81 | 10.58 |

**Table 4.4**
**Zn(II) - Lysine - Uracil - System**

| Volume of NaOH | pH | | | |
|---|---|---|---|---|
| | A | B | C | D |
| 0.0 | 2.94 | 2.74 | 2.73 | 2.98 |
| 0.2 | 3.00 | 2.84 | 2.83 | 3.19 |
| 0.4 | 3.27 | 2.97 | 2.96 | 3.65 |
| 0.6 | 4.07 | 3.15 | 3.14 | 6.88 |
| 0.8 | 10.14 | 3.4 | 3.48 | 7.49 |
| 1.0 | 10.54 | 6.77 | 6.03 | 7.60 |
| 1.2 | 10.85 | 8.84 | 7.51 | 7.69 |
| 1.4 | 10.99 | 9.40 | 7.69 | 7.80 |
| 1.6 | 11.03 | 9.87 | 7.80 | 7.92 |
| 1.8 | 11.08 | 10.23 | 7.88 | 8.09 |
| 2.0 | 11.15 | 10.47 | 8.48 | 8.39 |
| 2.2 | 11.20 | 10.64 | 8.96 | 8.74 |
| 2.4 | 11.24 | 10.78 | 9.41 | 9.04 |
| 2.6 | 11.28 | 10.89 | 9.82 | 9.33 |
| 2.8 | | 10.97 | 10.14 | 9.63 |
| 3.0 | | 11.05 | 10.38 | 9.93 |
| 3.2 | | 11.11 | 10.45 | 10.18 |

**Table - 4.5**
**Co(II) - Proline - Uracil - System**

| Volume Of NaOH | pH | | | |
|---|---|---|---|---|
| | A | B | C | D |
| 0.0 | 2.94 | 2.84 | 2.86 | 3.0 |
| 0.2 | 3.0 0 | 2.92 | 2.95 | 3.19 |
| 0.4 | 3.27 | 3.03 | 3.06 | 3.36 |
| 0.6 | 4.07 | 3.18 | 3.21 | 5.04 |
| 0.8 | 10.14 | 3.42 | 3.45 | 8.37 |
| 1.0 | 10.54 | 3.97 | 4.00 | 8.81 |
| 1.2 | 10.85 | 9.85 | 8.04 | 9.07 |
| 1.4 | 10.99 | 10.05 | 8.78 | 9.18 |
| 1.6 | 11.03 | 10.81 | 9.04 | 9.28 |
| 1.8 | 11.08 | 10.89 | 9.16 | 9.40 |
| 2.0 | 11.15 | 10.94 | 9.34 | 9.45 |
| 2.2 | 11.20 | 10.99 | 9.64 | 9.56 |
| 2.4 | 11.24 | 11.06 | 10.13 | 9.89 |
| 2.6 | 11.28 | 11.12 | 10.52 | 10.02 |
| 2.8 | | 11.16 | 10.77 | 10.37 |
| 3.0 | | | 10.95 | 10.67 |
| 3.2 | | | 11.02 | 10.73 |

**Table- 4.6**
**Ni (II) - Proline - Uracil - System**

| Volume Of NaOH | pH | | | |
|---|---|---|---|---|
| | A | B | C | D |
| 0.0 | 2.94 | 2.84 | 2.87 | 2.99 |
| 0.2 | 3.0 0 | 2.92 | 2.95 | 3.19 |
| 0.4 | 3.27 | 3.03 | 3.05 | 3.67 |
| 0.6 | 4.07 | 3.18 | 3.19 | 6.41 |
| 0.8 | 10.14 | 3.42 | 3.39 | 7.34 |
| 1.0 | 10.54 | 3.97 | 3.80 | 8.03 |
| 1.2 | 10.85 | 9.85 | 7.02 | 8.65 |
| 1.4 | 10.99 | 10.05 | 8.03 | 8.92 |
| 1.6 | 11.03 | 10.81 | 8.95 | 9.05 |
| 1.8 | 11.08 | 10.89 | 9.40 | 9.39 |
| 2.0 | 11.15 | 10.94 | 9.80 | 9.60 |
| 2.2 | 11.20 | 10.99 | 10.38 | 9.83 |
| 2.4 | 11.24 | 11.06 | 10.76 | 10.05 |
| 2.6 | 11.28 | 11.12 | 10.80 | 10.25 |
| 2.8 | | 11.16 | 10.86 | 10.41 |
| 3.0 | | 11.20 | 10.90 | 10.49 |
| 3.2 | | 11.24 | 10.95 | 10.53 |

**Table-4.7**
**Cu(II) - Proline - Uracil -System**

| Volume Of NaOH | pH | | | |
|---|---|---|---|---|
| | A | B | C | D |
| 0.0 | 2.94 | 2.84 | 2.89 | 3.01 |
| 0.2 | 3.0 0 | 2.92 | 2.98 | 3.09 |
| 0.4 | 3.27 | 3.03 | 3.01 | 3.25 |
| 0.6 | 4.07 | 3.18 | 3.24 | 3.51 |
| 0.8 | 10.14 | 3.42 | 3.37 | 3.99 |
| 1.0 | 10.54 | 3.97 | 3.82 | 4.81 |
| 1.2 | 10.85 | 9.85 | 7.04 | 5.75 |
| 1.4 | 10.99 | 10.05 | 8.04 | 7.11 |
| 1.6 | 11.03 | 10.81 | 8.96 | 7.62 |
| 1.8 | 11.08 | 10.89 | 9.39 | 8.32 |
| 2.0 | 11.15 | 10.94 | 9.86 | 9.26 |
| 2.2 | 11.20 | 10.99 | 10.78 | 9.88 |
| 2.4 | 11.24 | 11.06 | 10.82 | 10.42 |
| 2.6 | 11.28 | 11.12 | 10.80 | 10.50 |

**Table- 4.8**
**Zn (II) - Proline - Uracil - System**

| Volume Of NaOH | pH | | | |
|---|---|---|---|---|
| | A | B | C | D |
| 0.0 | 2.94 | 2.84 | 2.89 | 3.01 |
| 0.2 | 3.0 0 | 2.92 | 2.96 | 3.17 |
| 0.4 | 3.27 | 3.03 | 3.07 | 3.35 |
| 0.6 | 4.07 | 3.18 | 3.21 | 3.63 |
| 0.8 | 10.14 | 3.42 | 3.43 | 4.81 |
| 1.0 | 10.54 | 3.97 | 3.88 | 7.94 |
| 1.2 | 10.85 | 9.85 | 7.43 | 8.08 |
| 1.4 | 10.99 | 10.05 | 7.89 | 8.18 |
| 1.6 | 11.03 | 10.81 | 8.05 | 8.27 |
| 1.8 | 11.08 | 10.89 | 8.73 | 8.35 |
| 2.0 | 11.15 | 10.94 | 8.96 | 8.45 |
| 2.2 | 11.20 | 10.99 | 9.43 | 8.60 |
| 2.4 | 11.24 | 11.06 | 9.83 | 8.89 |
| 2.6 | 11.28 | 11.12 | 10.14 | 9.94 |
| 2.8 | | 11.16 | 10.41 | 9.42 |
| 3.0 | | 11.20 | 10.71 | 10.36 |
| 3.2 | | 11.24 | 10.75 | 10.42 |

**Table-4.9**
**Co(II) - Valine - Thymine - System**

| Volume Of NaOH | pH | | | |
|---|---|---|---|---|
| | A | B | C | D |
| 0.0 | 2.94 | 2.82 | 2.75 | 3.04 |
| 0.2 | 3.0 0 | 2.94 | 2.84 | 3.16 |
| 0.4 | 3.27 | 3.12 | 2.96 | 3.40 |
| 0.6 | 4.07 | 3.39 | 3.12 | 3.94 |
| 0.8 | 10.14 | 8.95 | 4.40 | 7.43 |
| 1.0 | 10.54 | 9.56 | 8.99 | 8.22 |
| 1.2 | 10.85 | 10.03 | 9.58 | 8.69 |
| 1.4 | 10.99 | 10.36 | 10.09 | 8.92 |
| 1.6 | 11.03 | 10.57 | 10.41 | 9.05 |
| 1.8 | 11.08 | 10.70 | 10.59 | 9.24 |
| 2.0 | 11.15 | 10.82 | 10.76 | 9.45 |
| 2.2 | 11.20 | 10.90 | 10.92 | 9.65 |
| 2.4 | 11.24 | 11.02 | 10.99 | 9.86 |
| 2.6 | 11.28 | 11.08 | 11.04 | 10.08 |
| 2.8 | | 11.12 | 11.10 | 10.29 |
| 3.0 | | 11.16 | 11.15 | 10.50 |
| 3.2 | | 11.20 | 11.20 | 10.61 |

**Table- 4.10**
**Ni(II) - Valine - Thymine - System**

| Volume Of NaOH | pH | | | |
|---|---|---|---|---|
| | A | B | C | D |
| 0.0 | 2.94 | 2.82 | 2.72 | 2.99 |
| 0.2 | 3.0 0 | 2.94 | 2.82 | 3.15 |
| 0.4 | 3.27 | 3.12 | 2.94 | 3.39 |
| 0.6 | 4.07 | 3.39 | 3.12 | 6.41 |
| 0.8 | 10.14 | 8.95 | 3.39 | 7.21 |
| 1.0 | 10.54 | 9.56 | 4.40 | 8.65 |
| 1.2 | 10.85 | 10.03 | 8.95 | 9.20 |
| 1.4 | 10.99 | 10.36 | 9.56 | 9.37 |
| 1.6 | 11.03 | 10.57 | 10.03 | 9.62 |
| 1.8 | 11.08 | 10.70 | 10.36 | 9.86 |
| 2.0 | 11.15 | 10.82 | 10.57 | 8.97 |
| 2.2 | 11.20 | 10.90 | 10.70 | 10.07 |
| 2.4 | 11.24 | 11.02 | 10.82 | 10.30 |
| 2.6 | 11.28 | 11.08 | 10.90 | 10.46 |
| 2.8 | | 11.12 | 11.02 | 10.62 |
| 3.0 | | 11.16 | 11.08 | 10.74 |
| 3.2 | | 11.20 | 11.12 | 10.78 |

**Table- 4.11**
**Cu(II) - Valine - Thymine - System**

| Volume Of NaOH | pH | | | |
|---|---|---|---|---|
| | A | B | C | D |
| 0.0 | 2.94 | 2.82 | 3.00 | 3.02 |
| 0.2 | 3.0 0 | 2.94 | 3.25 | 3.35 |
| 0.4 | 3.27 | 3.12 | 3.67 | 3.65 |
| 0.6 | 4.07 | 3.39 | 4.26 | 4.13 |
| 0.8 | 10.14 | 8.95 | 6.48 | 4.76 |
| 1.0 | 10.54 | 9.56 | 6.84 | 5.55 |
| 1.2 | 10.85 | 10.03 | 8.56 | 6.70 |
| 1.4 | 10.99 | 10.36 | 8.98 | 7.37 |
| 1.6 | 11.03 | 10.57 | 10.00 | 8.04 |
| 1.8 | 11.08 | 10.70 | 10.30 | 8.34 |
| 2.0 | 11.15 | 10.82 | 10.50 | 8.97 |
| 2.2 | 11.20 | 10.90 | 10.75 | 9.57 |
| 2.4 | 11.24 | 11.02 | 10.86 | 9.98 |
| 2.6 | 11.28 | 11.08 | 10.90 | 10.28 |
| 2.8 | | 11.12 | 10.98 | 10.51 |
| 3.0 | | 11.16 | 11.02 | 10.56 |
| 3.2 | | 11.20 | 10.75 | 10.60 |

**Table- 4.12**
**Zn(II) - Valine - Thymine - System**

| Volume Of NaOH | pH | | | |
|---|---|---|---|---|
| | A | B | C | D |
| 0.0 | 2.94 | 2.82 | 2.73 | 3.00 |
| 0.2 | 3.0 0 | 2.94 | 2.82 | 3.20 |
| 0.4 | 3.27 | 3.12 | 2.94 | 3.44 |
| 0.6 | 4.07 | 3.39 | 3.12 | 3.98 |
| 0.8 | 10.14 | 8.95 | 3.39 | 6.92 |
| 1.0 | 10.54 | 9.56 | 4.40 | 7.51 |
| 1.2 | 10.85 | 10.03 | 7.95 | 7.64 |
| 1.4 | 10.99 | 10.36 | 8.96 | 7.77 |
| 1.6 | 11.03 | 10.57 | 10.09 | 8.51 |
| 1.8 | 11.08 | 10.70 | 10.46 | 8.94 |
| 2.0 | 11.15 | 10.82 | 10.67 | 9.56 |
| 2.2 | 11.20 | 10.90 | 10.73 | 9.80 |
| 2.4 | 11.24 | 11.02 | 10.80 | 10.04 |
| 2.6 | 11.28 | 11.08 | 10.90 | 10.25 |
| 2.8 | | 11.12 | 10.96 | 10.50 |
| 3.0 | | 11.16 | 11.01 | 10.56 |
| 3.2 | | 11.20 | | 10.60 |

**Table 4.13**
**Co(II) - Asparagine -Thymine - System**

| Volume of NaOH | pH | | | |
|---|---|---|---|---|
| | A | B | C | D |
| 0.0 | 2.94 | 2.8 | 2.73 | 3.01 |
| 0.2 | 3.00 | 2.9 | 2.84 | 3.25 |
| 0.4 | 3.27 | 3.9 | 2.98 | 3.81 |
| 0.6 | 9.07 | 8.42 | 5.99 | 6.58 |
| 0.8 | 10.14 | 9.4 | 7.23 | 7.49 |
| 1.0 | 10.54 | 9.91 | 8.06 | 8.32 |
| 1.2 | 10.85 | 10.26 | 8.91 | 8.89 |
| 1.4 | 10.99 | 10.52 | 9.2 | 9.09 |
| 1.6 | 11.03 | 10.65 | 9.48 | 9.28 |
| 1.8 | 11.08 | 10.81 | 9.79 | 9.5 |
| 2.0 | 11.15 | 10.9 | 10.11 | 9.74 |
| 2.2 | 11.20 | 10.98 | 10.39 | 9.98 |
| 2.4 | 11.24 | 11.05 | 10.6 | 10.24 |
| 2.6 | 11.28 | 11.1 | 10.7 | 10.47 |
| 2.8 | | 11.15 | 10.87 | 10.65 |
| 3.0 | | 11.2 | 10.94 | 10.79 |
| 3.2 | | 11.24 | 11.0 | 10.90 |

**Table 4.14**
**Ni(II) - Asparagine - Thymine - System**

| Volume of NaOH | pH | | | |
|---|---|---|---|---|
| | A | B | C | D |
| 0.0 | 2.94 | 2.8 | 2.75 | 2.99 |
| 0.2 | 3.00 | 2.9 | 2.83 | 3.2 |
| 0.4 | 3.27 | 3.9 | 2.96 | 3.68 |
| 0.6 | 9.07 | 8.42 | 3.15 | 5.54 |
| 0.8 | 10.14 | 9.4 | 5.12 | 6.44 |
| 1.0 | 10.54 | 9.91 | 6.22 | 7.5 |
| 1.2 | 10.85 | 10.26 | 7.13 | 8.92 |
| 1.4 | 10.99 | 10.52 | 9.04 | 9.26 |
| 1.6 | 11.03 | 10.65 | 9.86 | 9.53 |
| 1.8 | 11.08 | 10.81 | 10.2 | 9.79 |
| 2.0 | 11.15 | 10.9 | 10.48 | 10.09 |
| 2.2 | 11.20 | 10.98 | 10.63 | 10.29 |
| 2.4 | 11.24 | 11.05 | 10.74 | 10.5 |
| 2.6 | 11.28 | 11.1 | 10.8 | 10.64 |
| 2.8 | | 11.15 | 10.85 | 10.75 |
| 3.0 | | 11.2 | 10.9 | 10.83 |
| 3.2 | | 11.24 | 10.94 | 10.92 |

**Table - 4.15**
**Cu(II) - Asparagine -Thymine - System**

| Volume of NaOH | pH | | | |
|---|---|---|---|---|
| | A | B | C | D |
| 0.0 | 2.94 | 2.8 | 2.79 | 2.96 |
| 0.2 | 3.00 | 2.9 | 2.85 | 3.14 |
| 0.4 | 3.27 | 3.9 | 2.91 | 3.41 |
| 0.6 | 9.07 | 8.42 | 3.09 | 3.86 |
| 0.8 | 10.14 | 9.4 | 3.35 | 4.62 |
| 1.0 | 10.54 | 9.91 | 4.46 | 6.3 |
| 1.2 | 10.85 | 10.26 | 8.22 | 7.43 |
| 1.4 | 10.99 | 10.52 | 8.87 | 8.56 |
| 1.6 | 11.03 | 10.65 | 9.61 | 9.35 |
| 1.8 | 11.08 | 10.81 | 10.24 | 9.77 |
| 2.0 | 11.15 | 10.9 | 10.55 | 10.09 |
| 2.2 | 11.20 | 10.98 | 10.73 | 10.34 |
| 2.4 | 11.24 | 11.05 | 10.86 | 10.52 |
| 2.6 | 11.28 | 11.1 | 10.96 | 10.68 |
| 2.8 | | 11.15 | 11.04 | 10.8 |
| 3.0 | | 11.2 | 11.1 | 10.9 |
| 3.2 | | 11.24 | 11.15 | 10.97 |
| 3.4 | | | | 11.04 |

**Table - 4.16**
**Zn(II) - Aspagine - Thymine- System**

| Volume of NaOH | pH | | | |
|---|---|---|---|---|
| | A | B | C | D |
| 0.0 | 2.94 | 2.8 | 2.74 | 3.01 |
| 0.2 | 3.00 | 2.9 | 2.84 | 3.24 |
| 0.4 | 3.27 | 3.9 | 2.98 | 3.81 |
| 0.6 | 9.07 | 8.42 | 3.51 | 3.99 |
| 0.8 | 10.14 | 9.4 | 5.58 | 6.3 |
| 1.0 | 10.54 | 9.91 | 7.75 | 7.09 |
| 1.2 | 10.85 | 10.26 | 7.9 | 7.64 |
| 1.4 | 10.99 | 10.52 | 8.03 | 7.8 |
| 1.6 | 11.03 | 10.65 | 8.24 | 7.96 |
| 1.8 | 11.08 | 10.81 | 8.54 | 8.12 |
| 2.0 | 11.15 | 10.9 | 8.91 | 8.35 |
| 2.2 | 11.20 | 10.98 | 9.3 | 8.65 |
| 2.4 | 11.24 | 11.05 | 9.71 | 8.97 |
| 2.6 | 11.28 | 11.1 | 9.78 | 9.23 |
| 2.8 | | 11.15 | 9.86 | 9.53 |
| 3.0 | | 11.2 | 10.09 | 9.85 |
| 3.2 | | 11.24 | 10.14 | 9.89 |

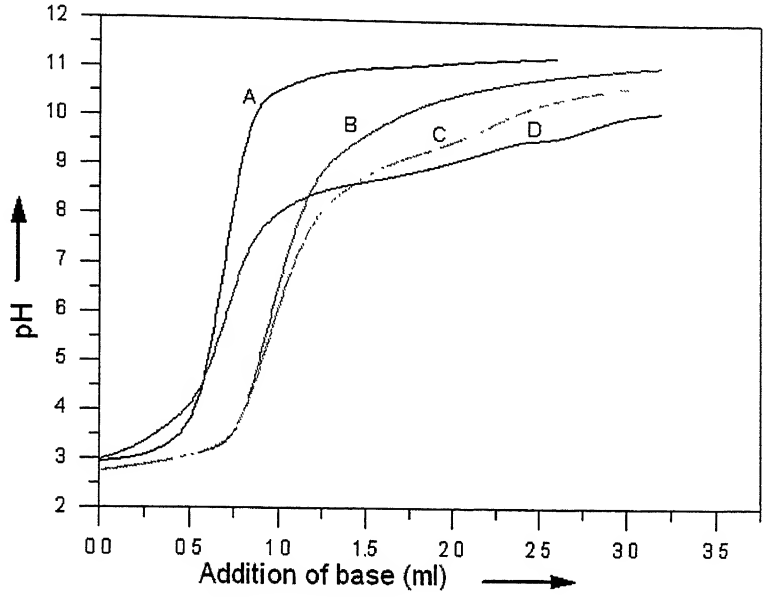



Fig 4.1- Potentiometric titration Curves of 1:1:1 Co(II)-Lysine-Uracil system; (A) Acid (B) Lysine (C) Co(II)-Lysine (D) Co(II)-Lysine-Uracil

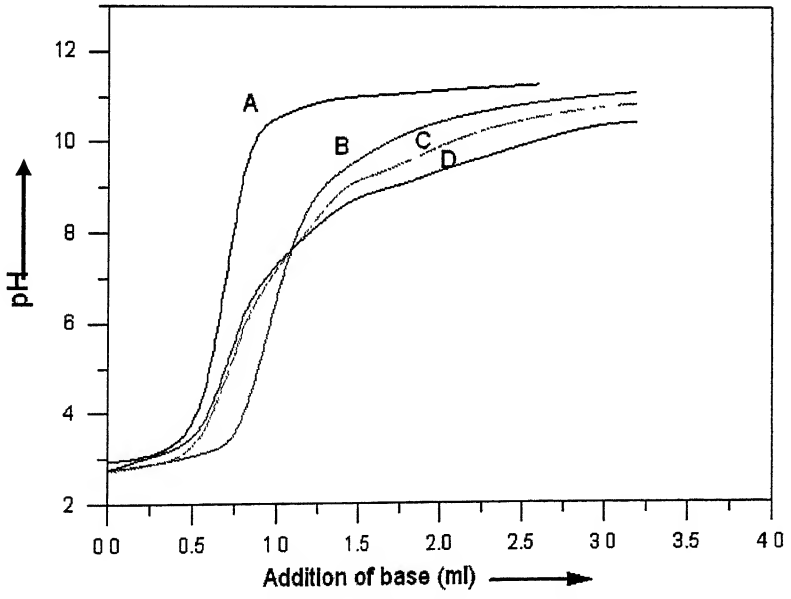



Fig 4.2- Potentiometric titration Curves of 1:1:1 Ni(II)-Lysine-Uracil system; (A) Acid (B) Lysine (C) Ni(II)-Lysine (D) Ni(II)-Lysine-Uracil

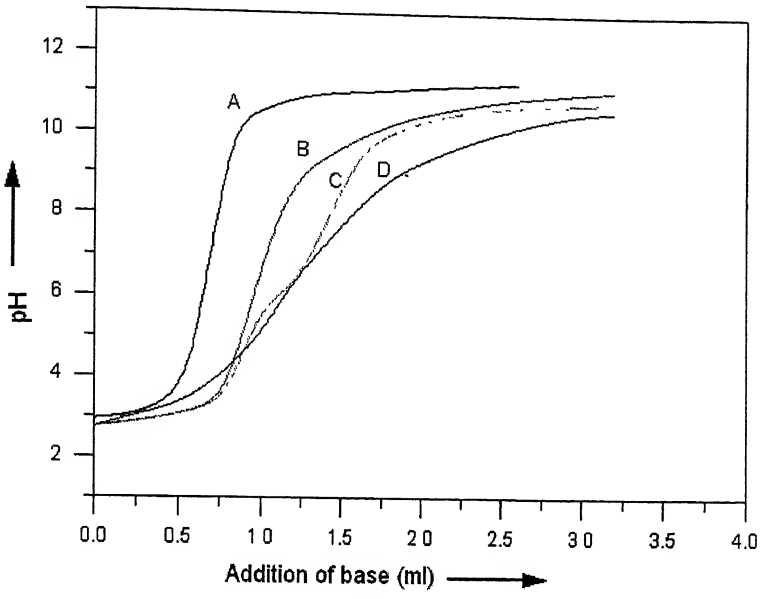



Fig 4.3- Potentiometric titration Curves of 1:1:1 Cu(II)-Lysine-Uracil system; (A) Acid (B) Lysine (C) Cu(II)-Lysine (D) Cu(II)-Lysine-Uracil

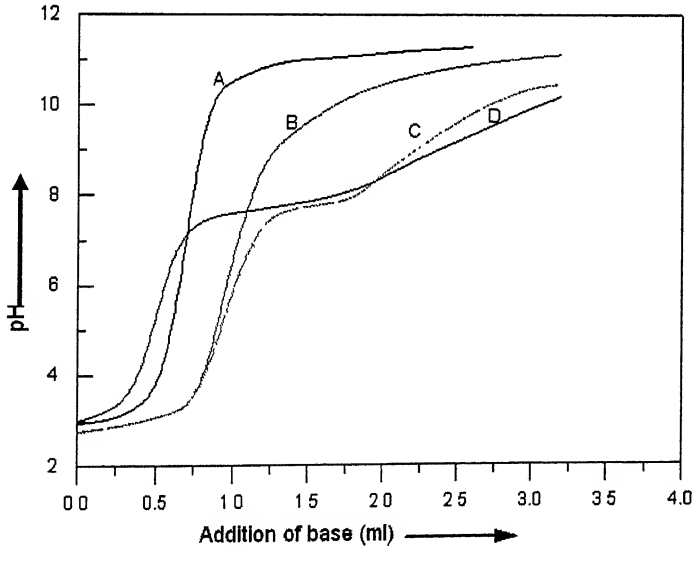



Fig 4.4- Potentiometric titration Curves of 1:1:1 Zn(II)-Lysine-Uracil system; (A) Acid (B) Lysine (C) Zn(II)-Lysine (D) Zn(II)-Lysine-Uracil

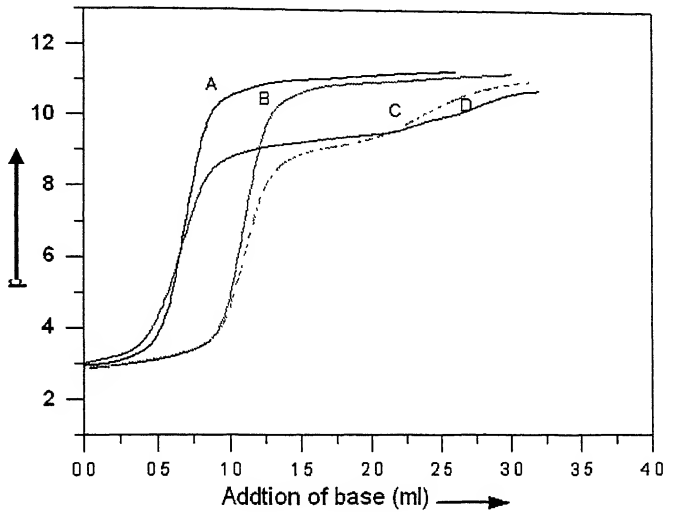



Fig 4.5- Potentiometric titration Curves of 1:1:1 Co(II)-Proline-Uracil system; (A) Acid (B) Proline (C) Co(II)-Proline (D) Co(II)-Proline-Uracil

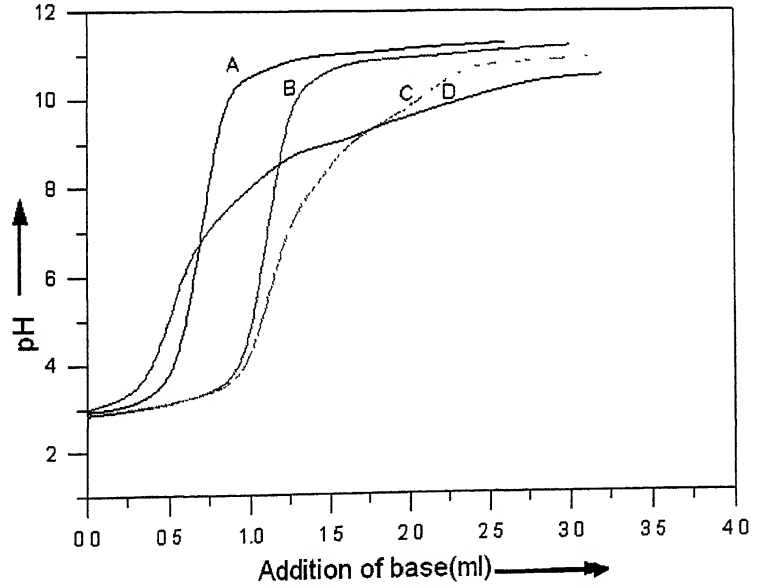



Fig 4.6- Potentiometric titration Curves of 1:1:1 Ni(II)-Proline-Uracil system; (A) Acid (B) Proline (C) Ni(II)-Proline (D) Ni(II)-Proline-Uracil

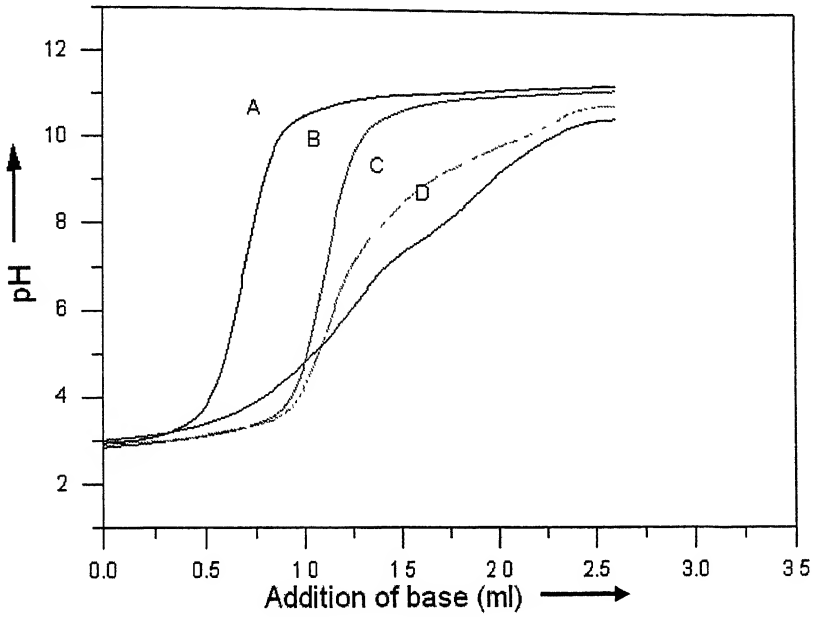



Fig 4.7- Potentiometric titration Curves of 1:1:1 Cu(II)-Proline-Uracil system; (A) Acid (B) Proline (C) Cu(II)-Proline (D) Cu(II)-Proline-Uracil

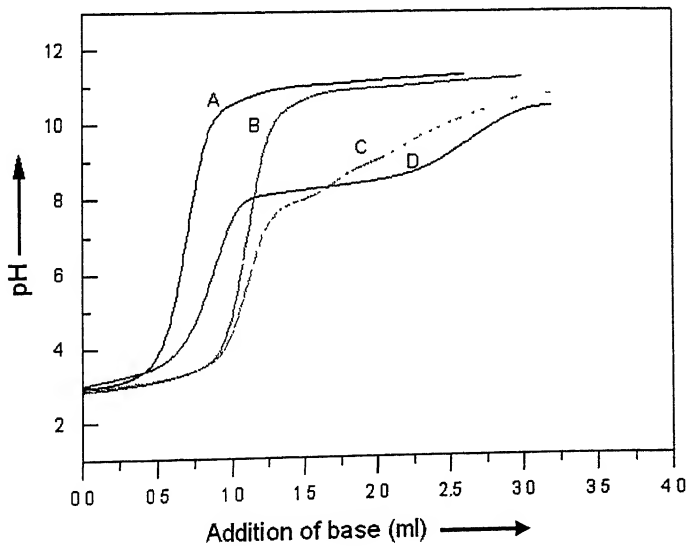



Fig 4.8- Potentiometric titration Curves of 1:1:1 Zn(II)-Proline-Uracil system; (A) Acid (B) Proline (C) Zn(II)-Proline (D) Zn(II)-Proline-Uracil

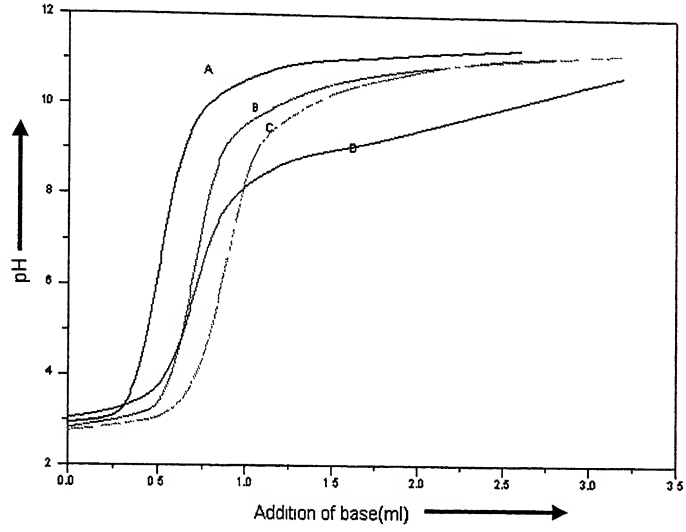



Fig 4.9- Potentiometric titration Curves of 1:1:1 Co(II)-Valine-Thymine system; (A) Acid (B) Valine (C) Co(II)-Valine (D) Co(II)-Valine-Thymine

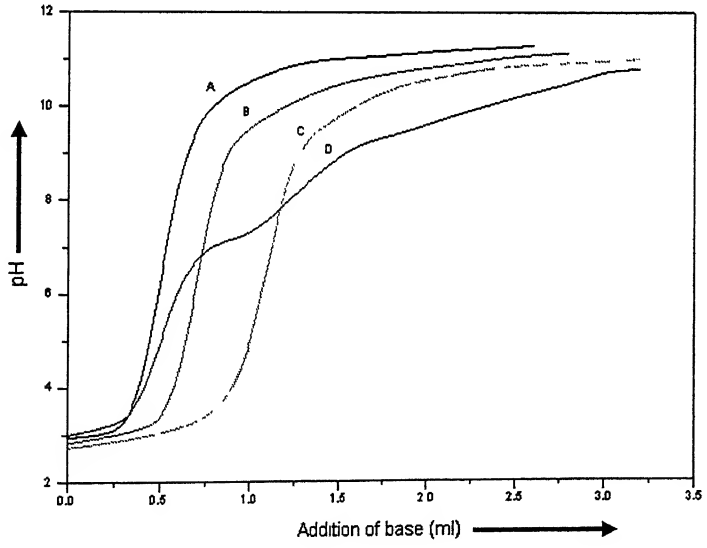



Fig 4.10- Potentiometric titration Curves of 1:1:1 Ni(II)-Valine-Thymine system; (A) Acid (B) Valine (C) Ni(II)-Valine (D) Ni(II)-Valine-Thymine

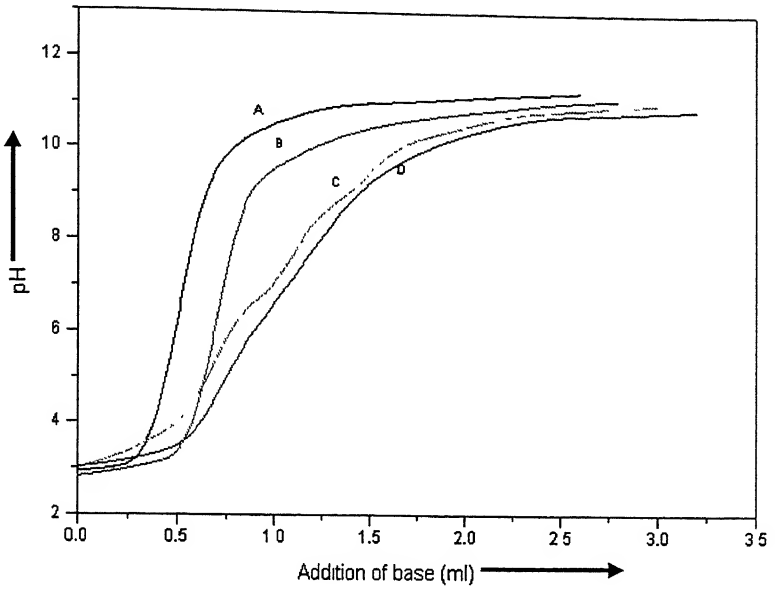



Fig 4.11- Potentiometric titration Curves of 1:1:1 Cu(II)-Valine-Thymine system; (A) Acid (B) Valine (C) Cu(II)-Valine (D) Cu(II)-Valine-Thymine

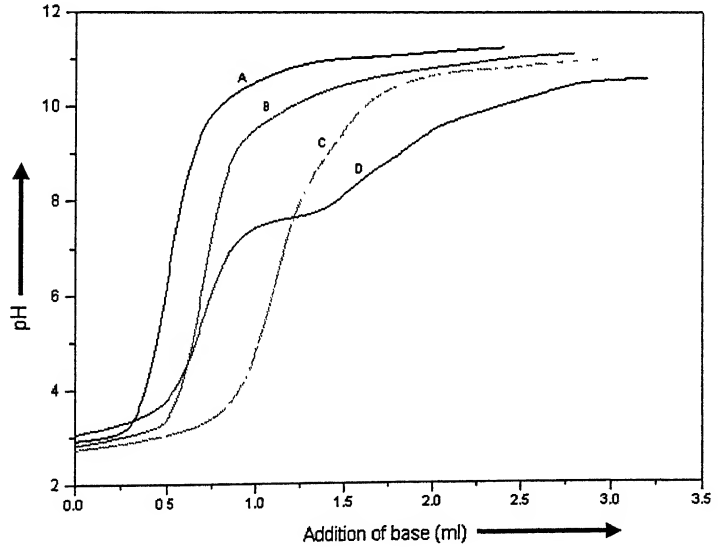



Fig 4.12- Potentiometric titration Curves of 1:1:1 Zn(II)-Valine-Thymine system; (A) Acid (B) Valine (C) Zn(II)-Valine (D) Zn(II)-Valine-Thymine

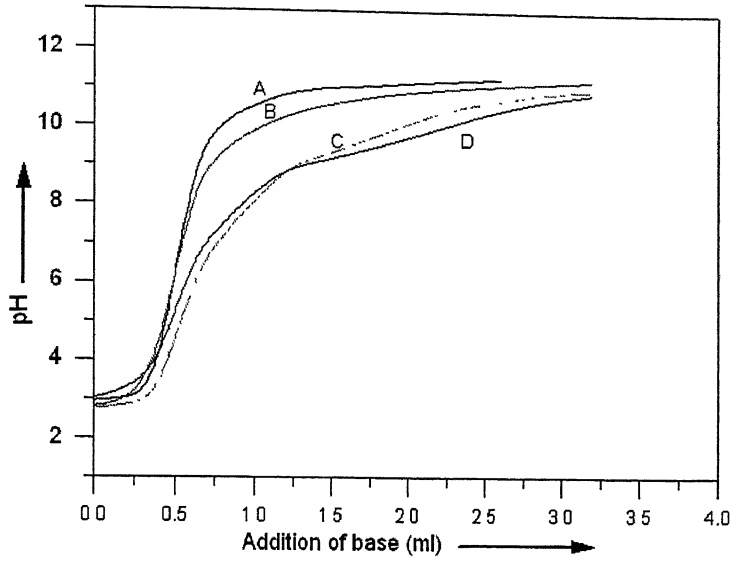



Fig 4.13- Potentiometric titration Curves of 1:1:1 Co(II)-Asparagine-Thymine system; (A) Acid (B)Asparagine (C) Co(II)-Asparagine (D) Co(II)-Asparagine-Thymine

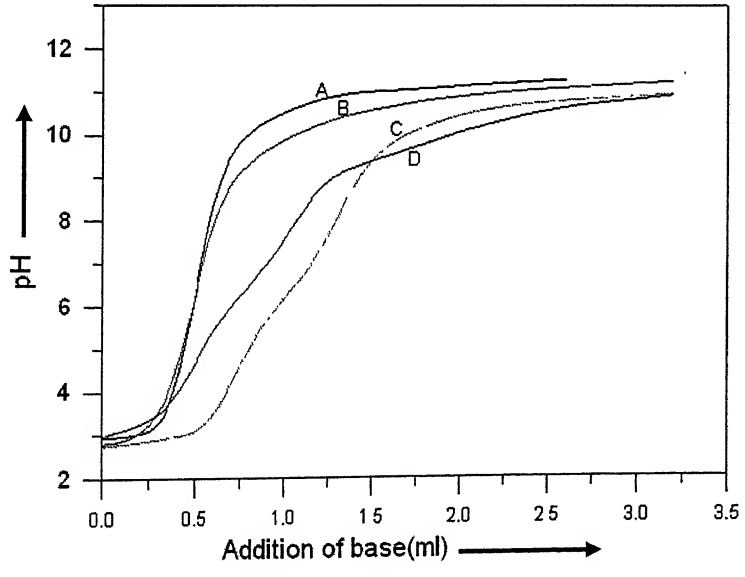



Fig 4.14- Potentiometric titration Curves of 1:1:1 Ni(II)-Asparagine-Thymine system; (A) Acid (B)Asparagine (C) Ni(II)-Asparagine (D) Ni(II)-Asparagine-Thymine

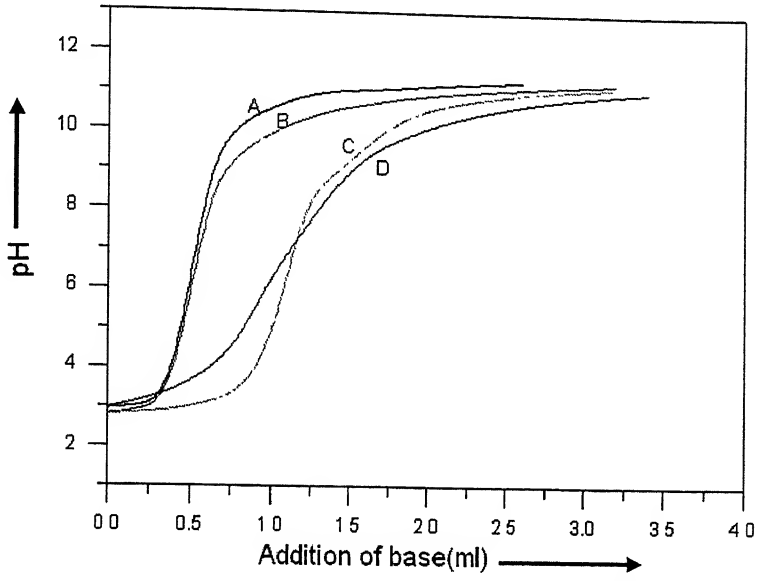



Fig 4.15- Potentiometric titration Curves of 1:1:1 Cu(II)-Asparagine-Thymine system; (A) Acid (B)Asparagine (C) Cu(II)-Asparagine (D) Cu(II)-Asparagine-Thymine

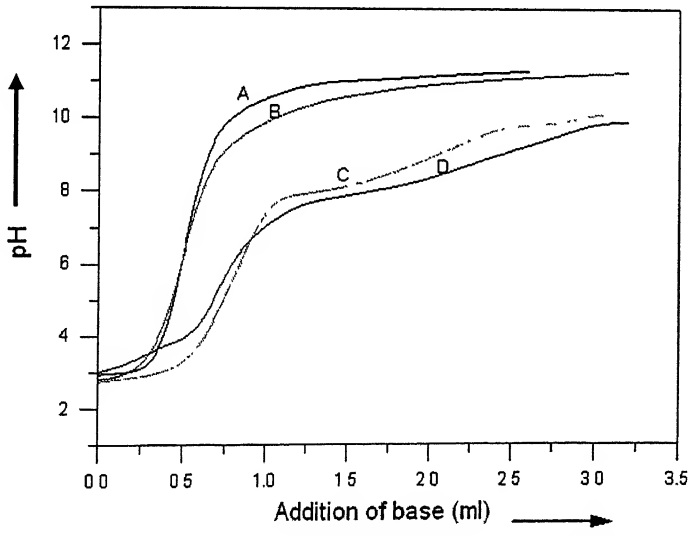



Fig 4.16- Potentiometric titration Curves of 1:1:1 Zn(II)-Asparagine-Thymine system; (A) Acid (B)Asparagine (C) Zn(II)-Asparagine (D) Zn(II)-Asparagine-Thymine

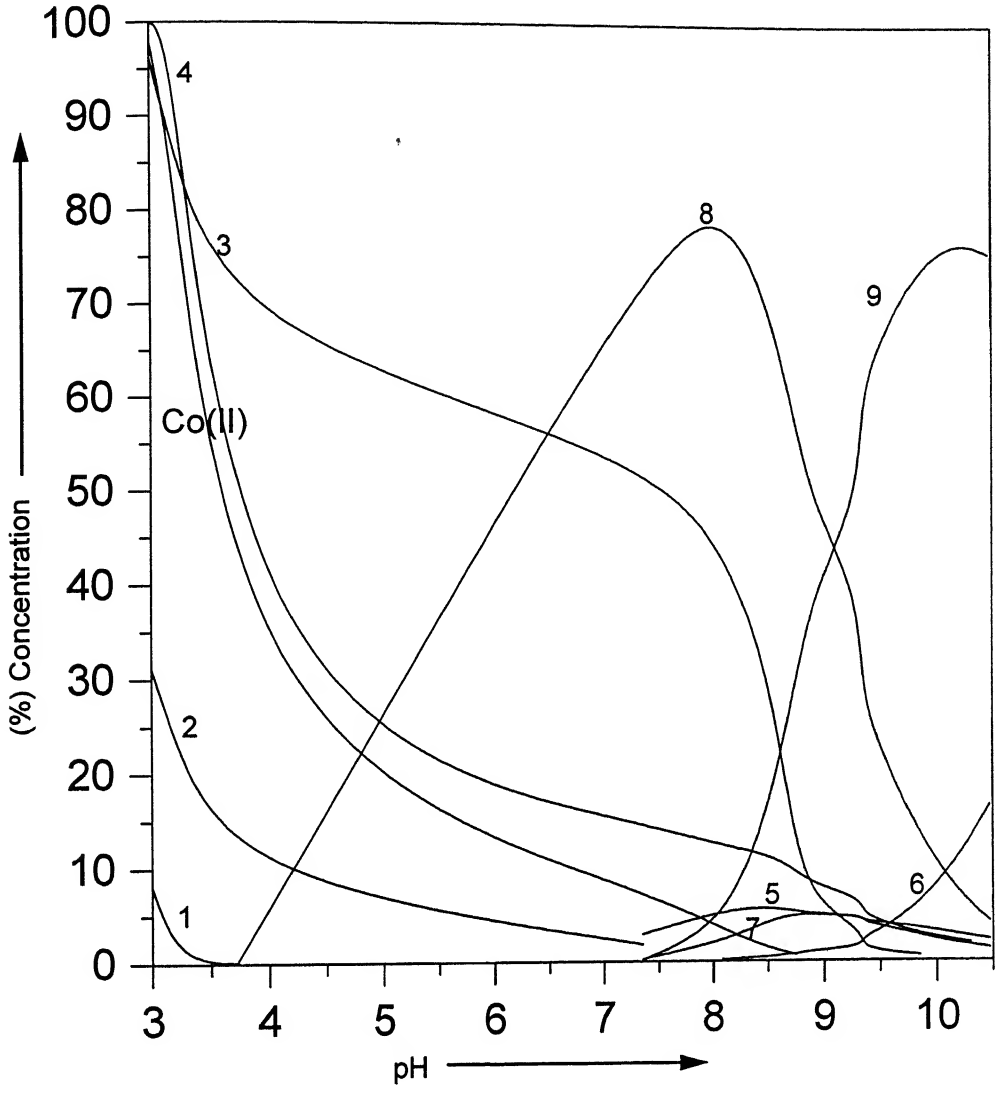



Fig.4.17- Distribution Curves of 1:1:1 Co(II)-Lysine-Uracil system; (I) $AH_3$ (2) $AH_2$ (3) AH (4) BH (5) $Co(OH)^+$ (6) $Co(OH)_2$ (7) CoA (8) CoB (9) CoAB

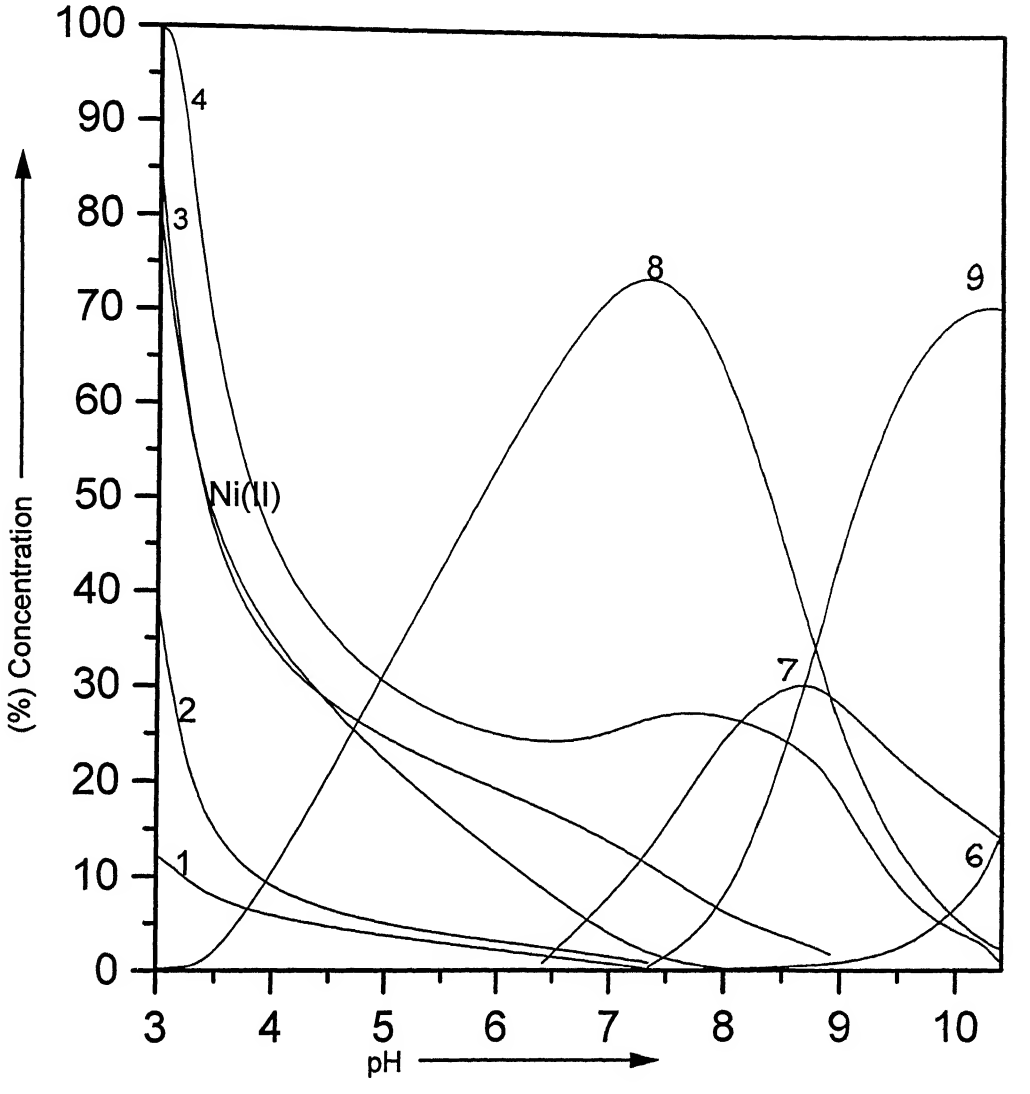



Fig .4.18- Distribution Curves of 1:1:1 Ni(II)-Lysine-Uracil system; (I) $AH_3$ (2) $AH_2$ (3) AH (4) BH (5) $Ni(OH)^+$ (6) $Ni(OH)_2$ (7) NiA (8) NiB (9) NiAB

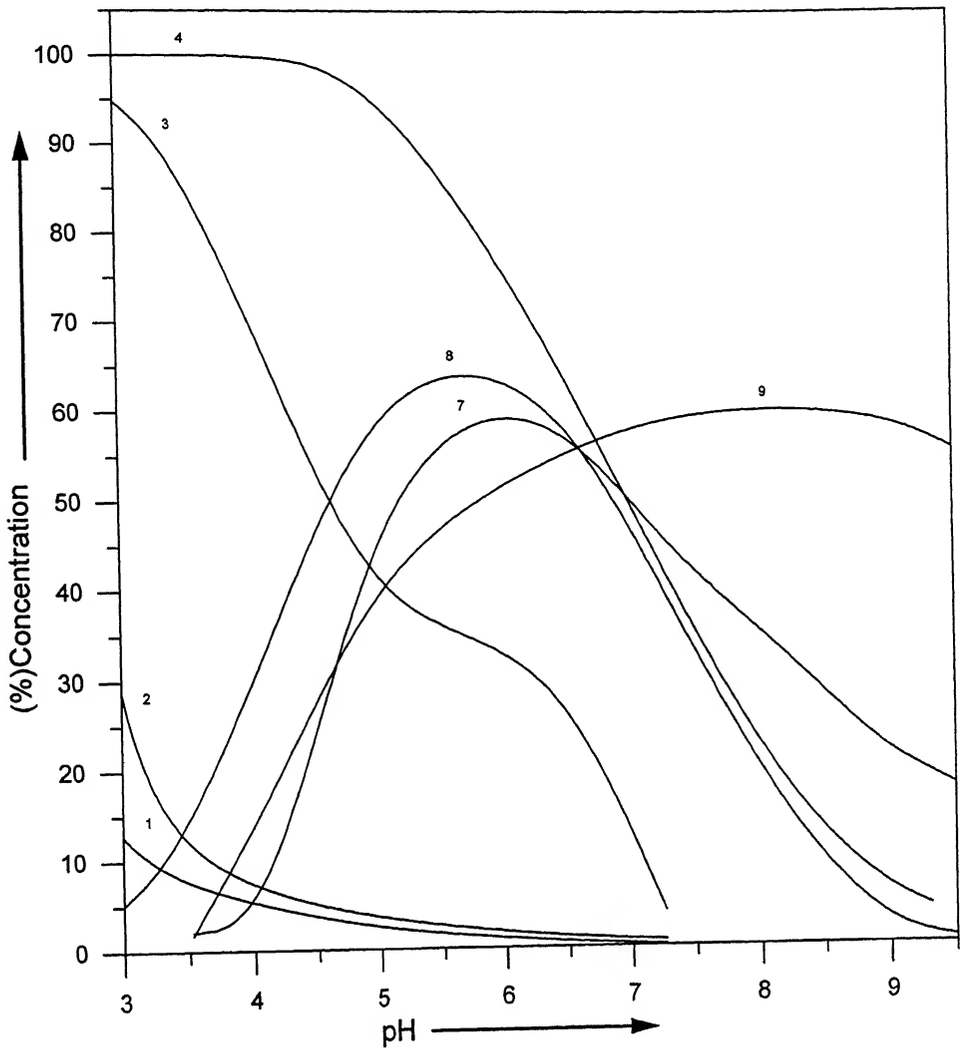



Fig 4.19- Distribution Curves of 1:1:1 Cu(II)-Lysine-Uracil system;(I) $AH_3$ (2) $AH_2$ (3) AH (4) BH (5) $Cu(OH)^+$ (6) $Cu(OH)_2$ (7) CuA (8) CuB (9) CuAB

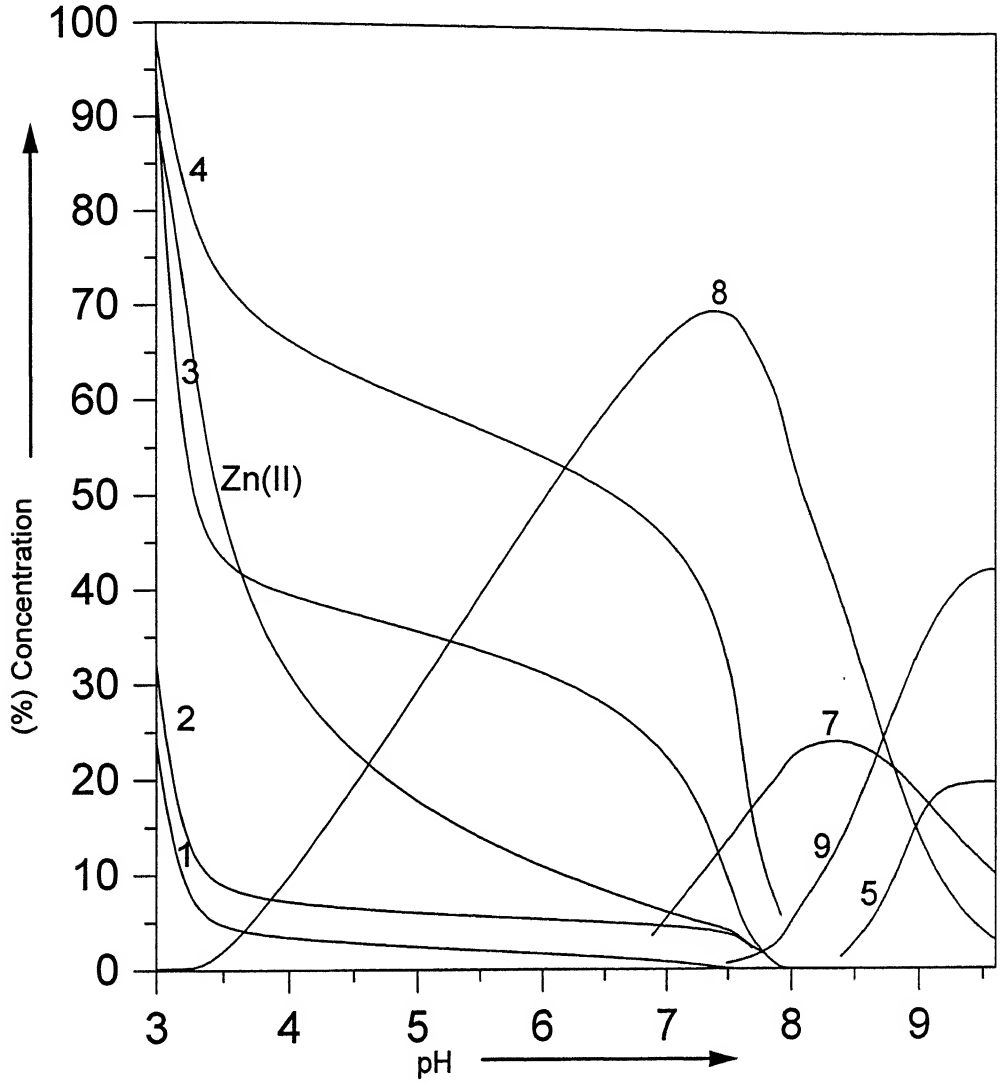



Fig.4.20- Distribution Curves of 1:1:1 Zn(II)-Lysine-Uracil system (I) $AH_3$ (2) $AH_2$ (3) AH (4) BH (5) $Zn(OH)^+$ (6) $Zn(OH)_2$ (7) ZnA (8) ZnB (9) ZnAB

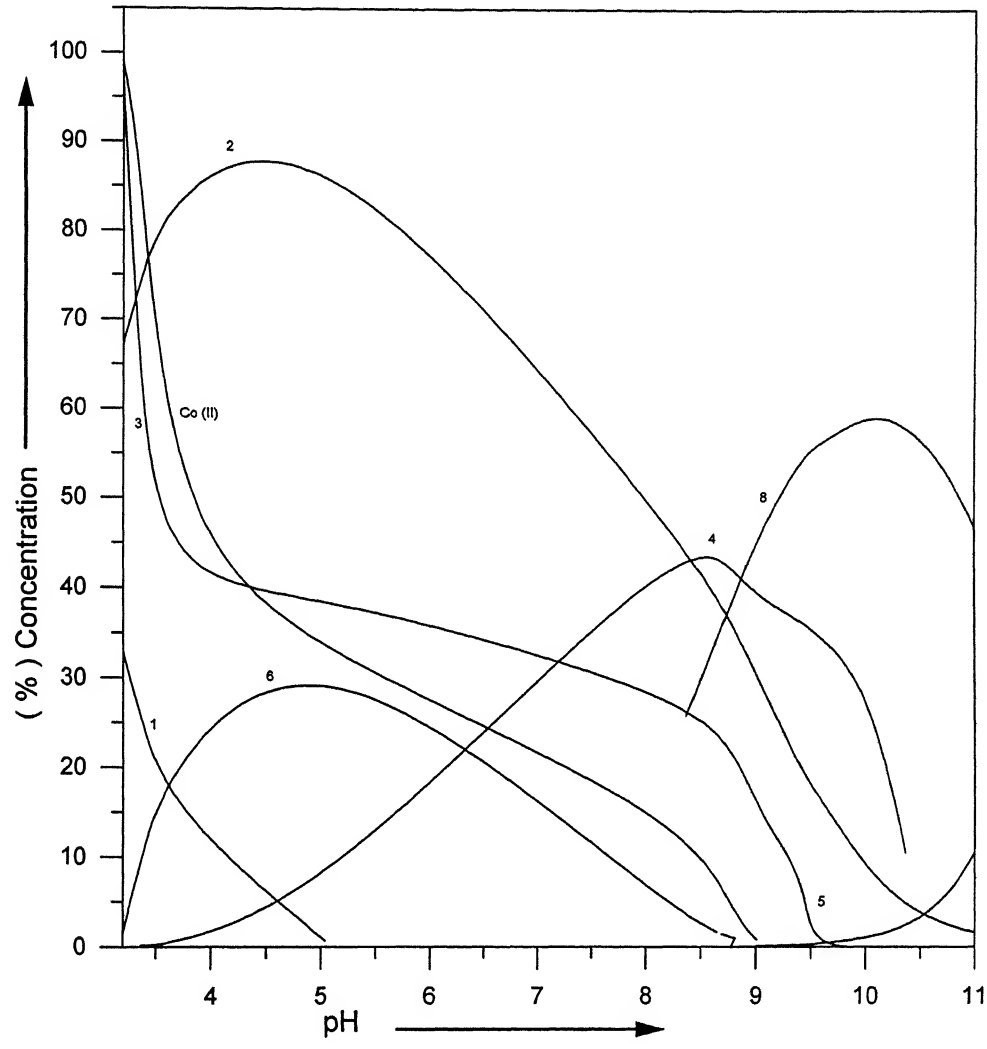



Fig.4.21- Distribution Curves of 1:1:1 Co(II)-Proline-Uracil system; (I) $AH_2$ (2) AH (3) BH (4) $Co(OH)^+$ (5) $Co(OH)_2$ (6) CoA (7) CoB (8) CoAB

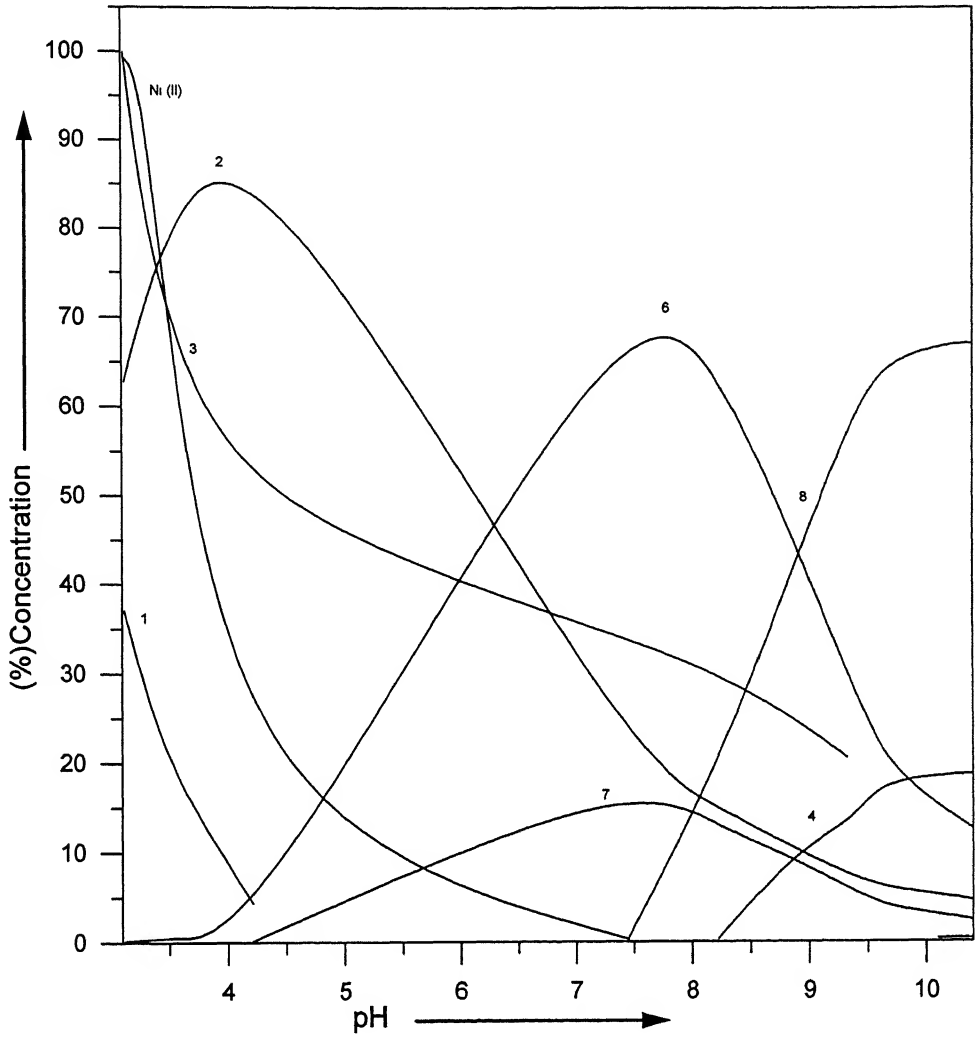



Fig. 4.22-Distribution Curves of 1:1:1 Ni(II)-Proline-Uracil system;(I) $AH_2$ (2) AH (3) BH(4) $Ni(OH)^+$ (5) $Ni(OH)_2$ (6) NiA (7) NiB (8) NiAB

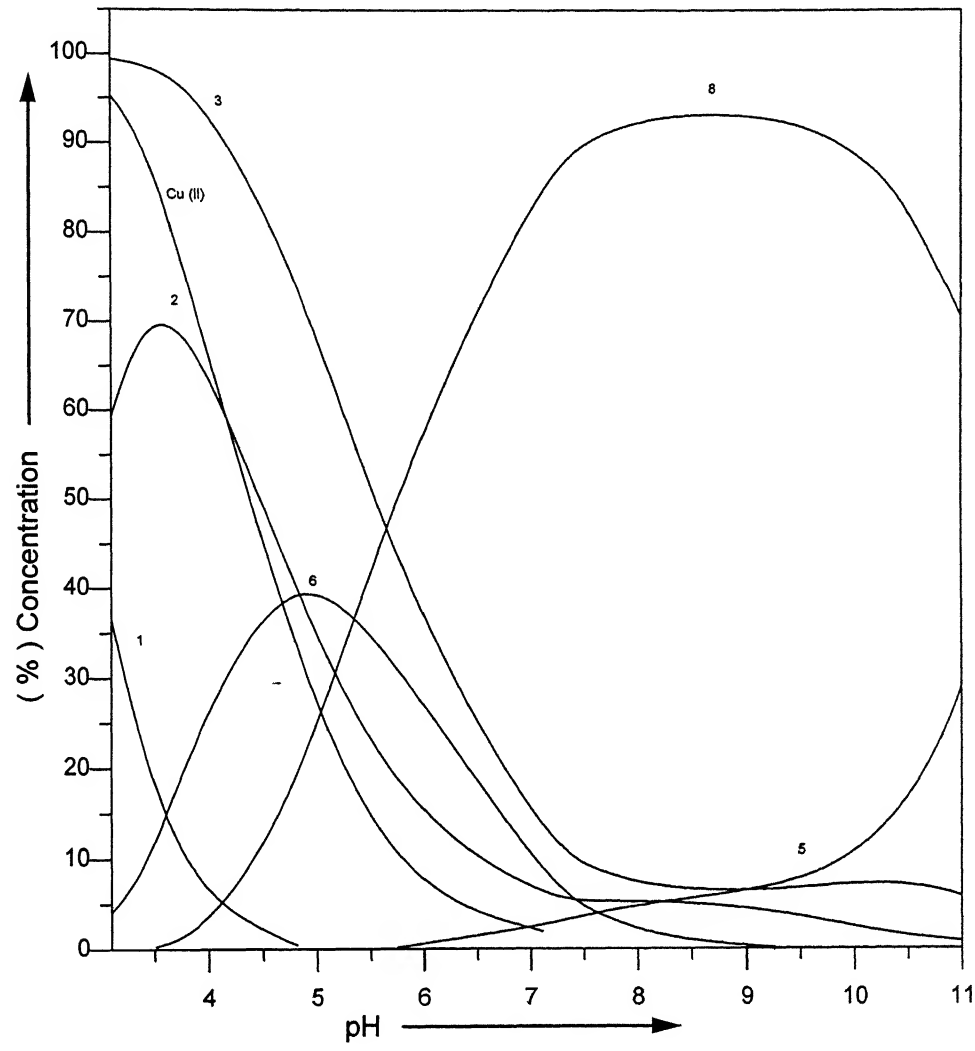



Fig .4.23- Distribution Curves of 1:1:1 Cu(II)-Proline-Uracil system; (I) $AH_2$ (2) AH (3) BH(4) $Cu(OH)^+$ (5) $Cu(OH)_2$ (6) CuA (7) CuB (8) CuAB

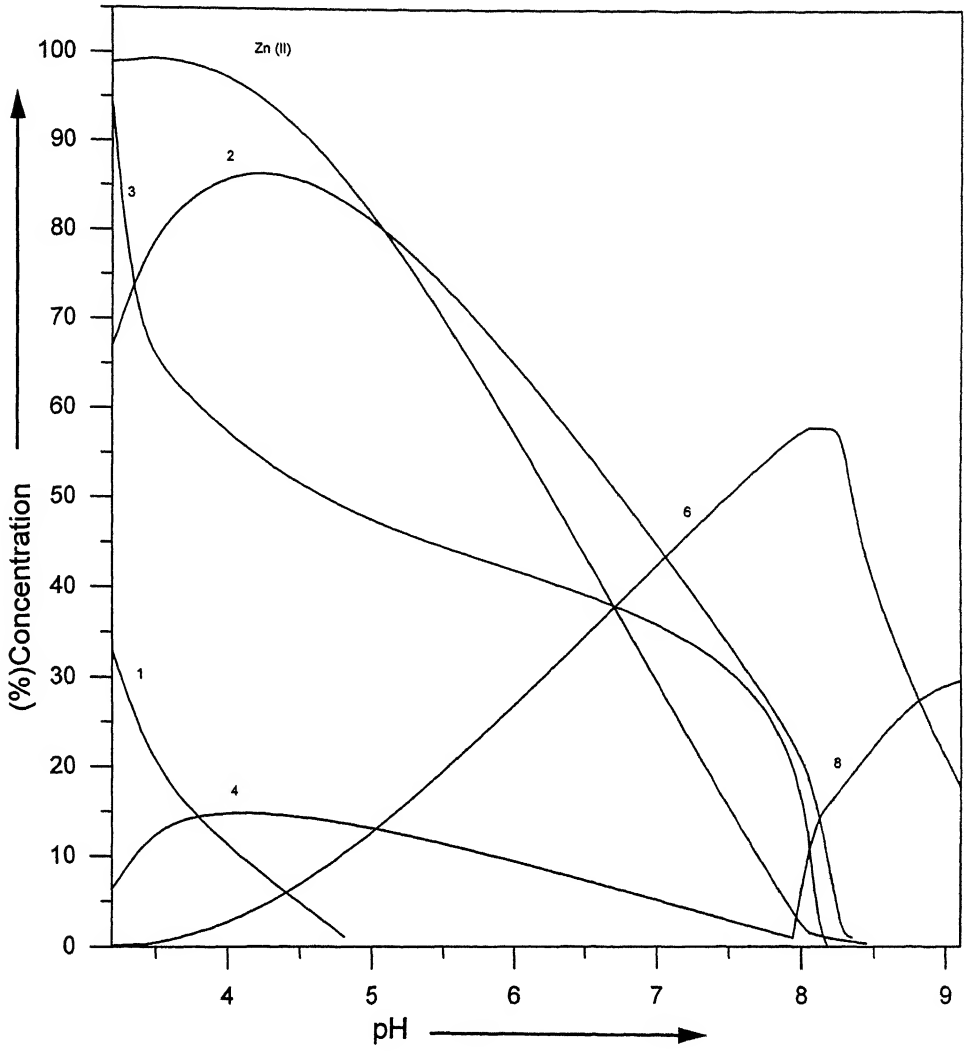



Fig.4.24- Distribution Curves of 1:1:1 Zn(II)-Proline-Uracil system; (I) $AH_2$ (2) AH (3) BH (4) $Zn(OH)^+$ (5) $Zn(OH)_2$ (6) ZnA (7) ZnB (8) ZnAB

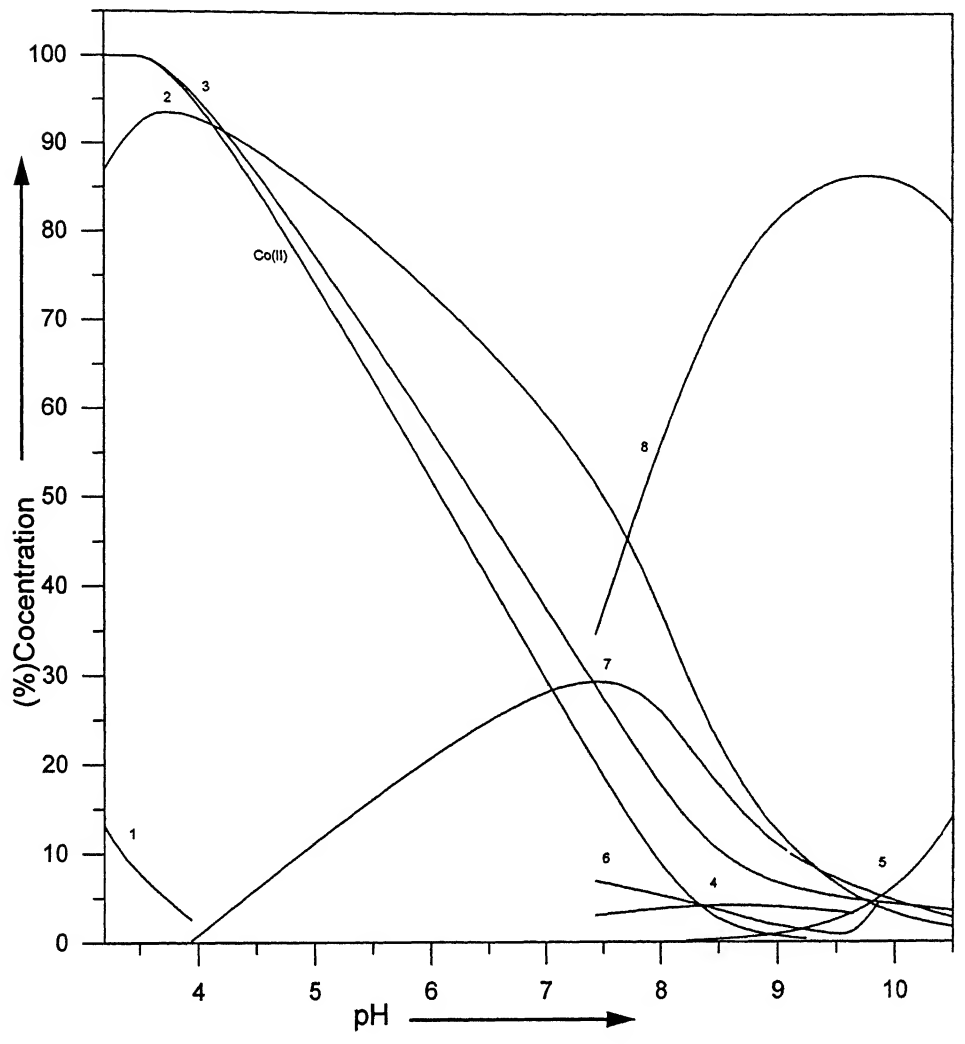



Fig.4.25- Distribution Curves of 1:1:1 Co(II)-Valine-Thymine system; (I) $AH_2$ (2) AH (3) BH (4) $Co(OH)^+$ (5) $Co(OH)_2$ (6) CoA (7) CoB (8) CoAB

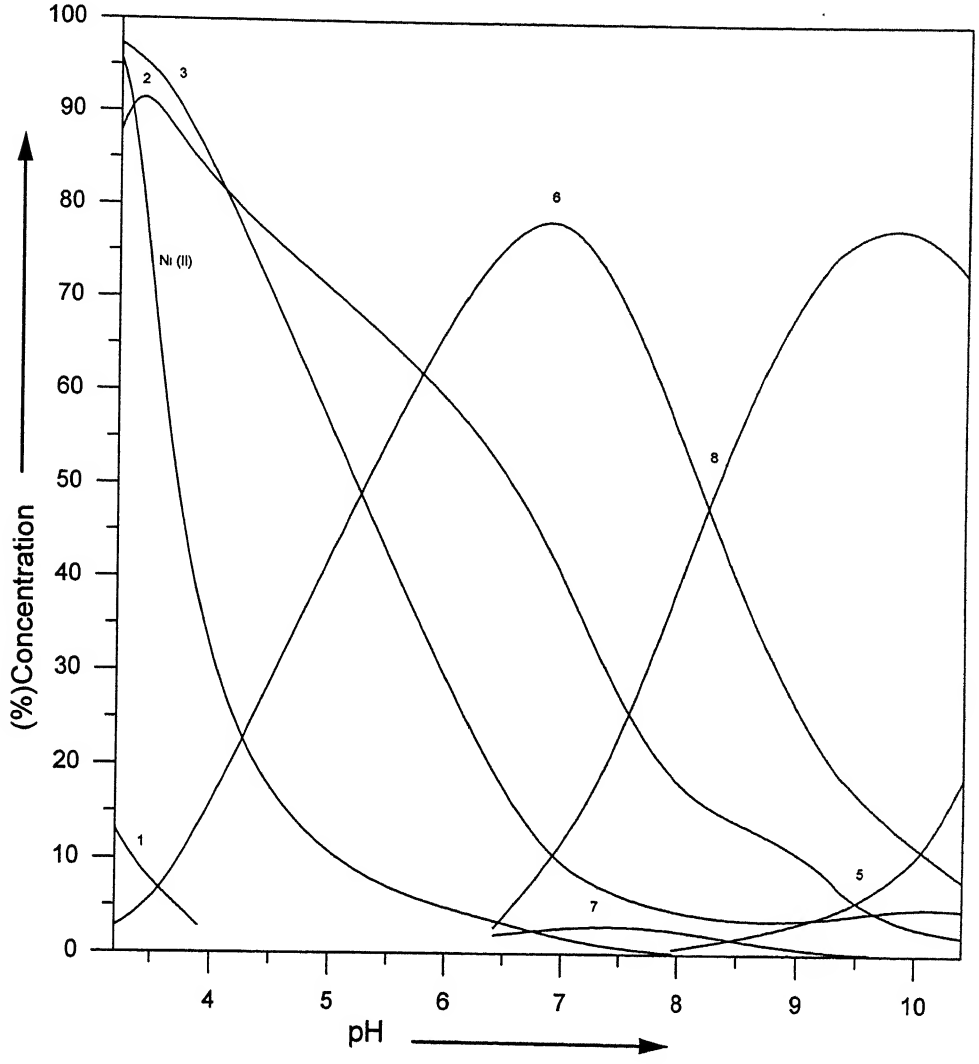



Fig.4.26- Distribution Curves of 1:1:1 Ni(II)-Valine-Thymine system; (I) $AH_2$ (2) AH (3) BH (4) $Ni(OH)^+$ (5) $Ni(OH)_2$ (6) NiA (7) NiB (8) NiAB

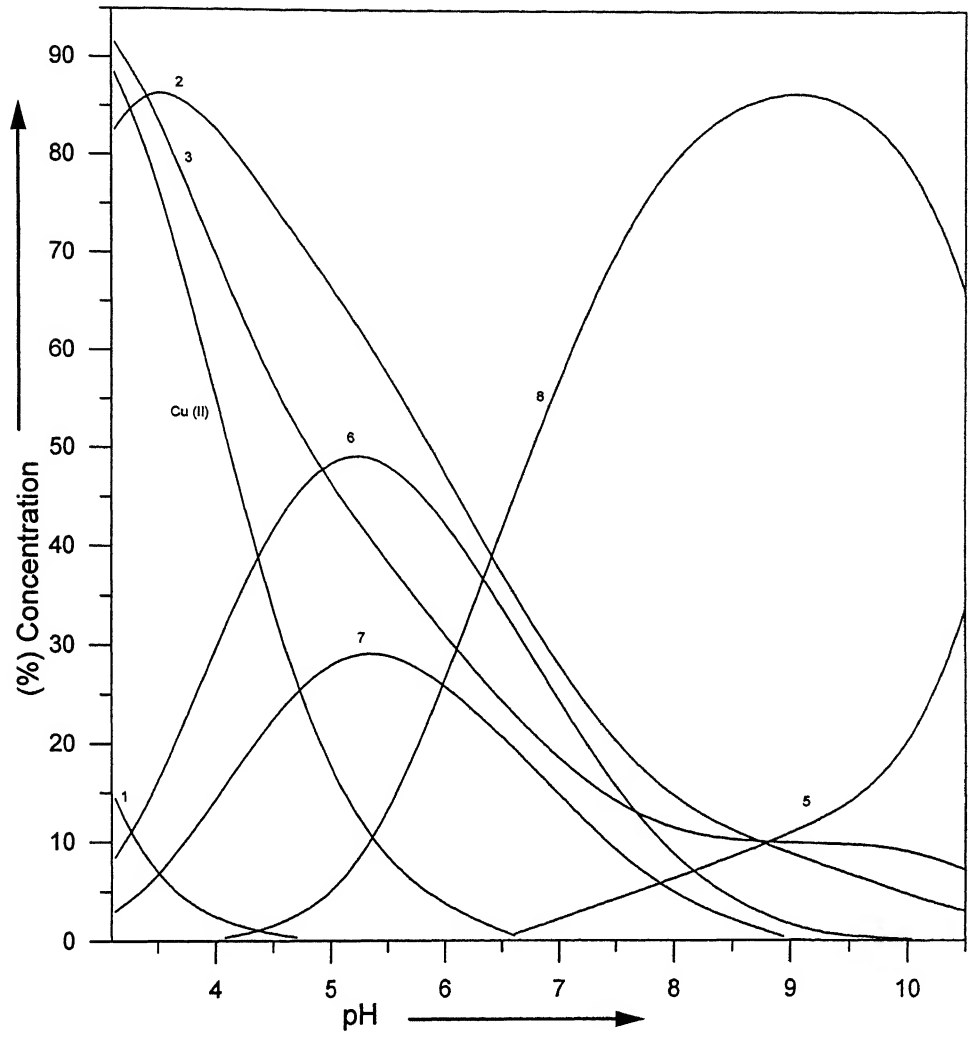



Fig.4.27- Distribution Curves of 1:1:1 Cu(II)-Valine-Thymine system; (I) $AH_2$ (2) AH (3) BH (4) $Cu(OH)^+$ (5) $Cu(OH)_2$ (6) CuA (7) CuB (8) CuAB

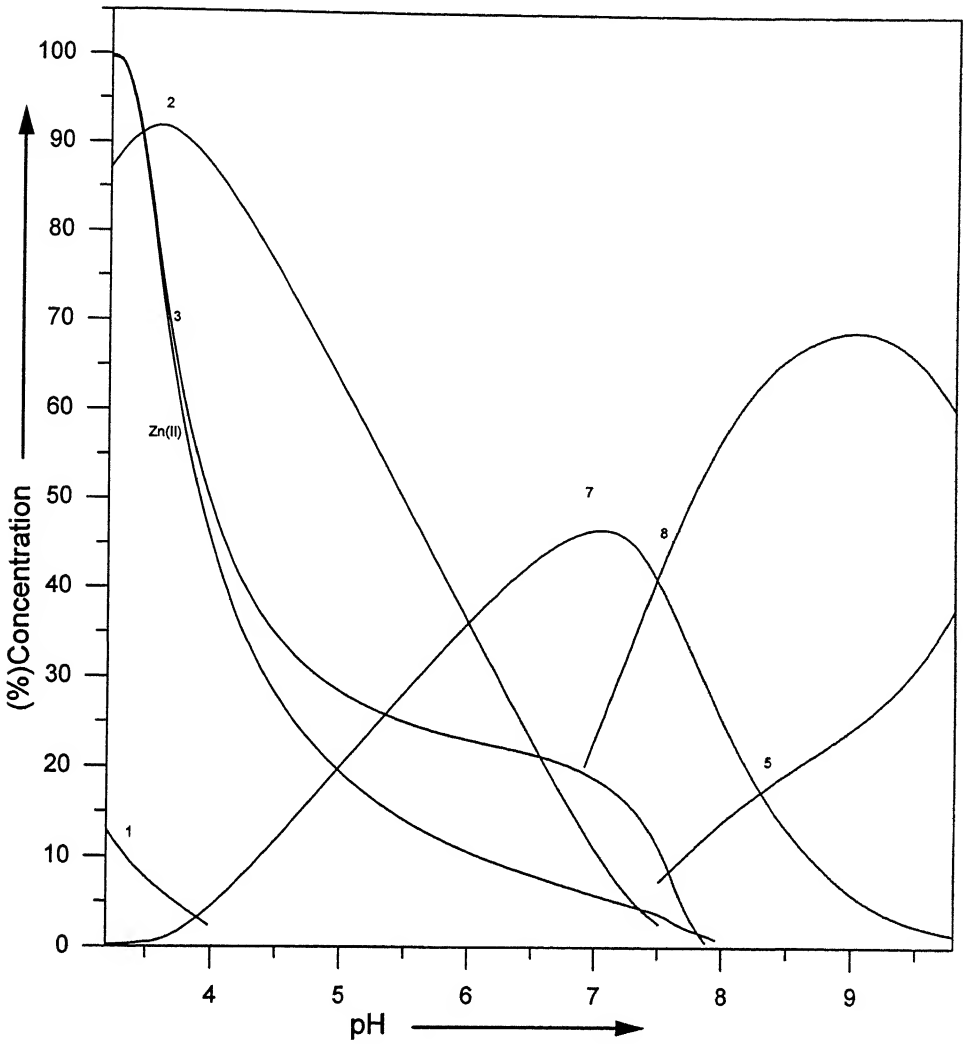



Fig.4.28- Distribution Curves of 1:1:1 Zn(II)-Valine-Thymine system; (I) $AH_2$ (2) AH (3) BH (4) $Zn(OH)^+$ (5) $Zn(OH)_2$ (6) ZnA (7) ZnB (8) ZnAB

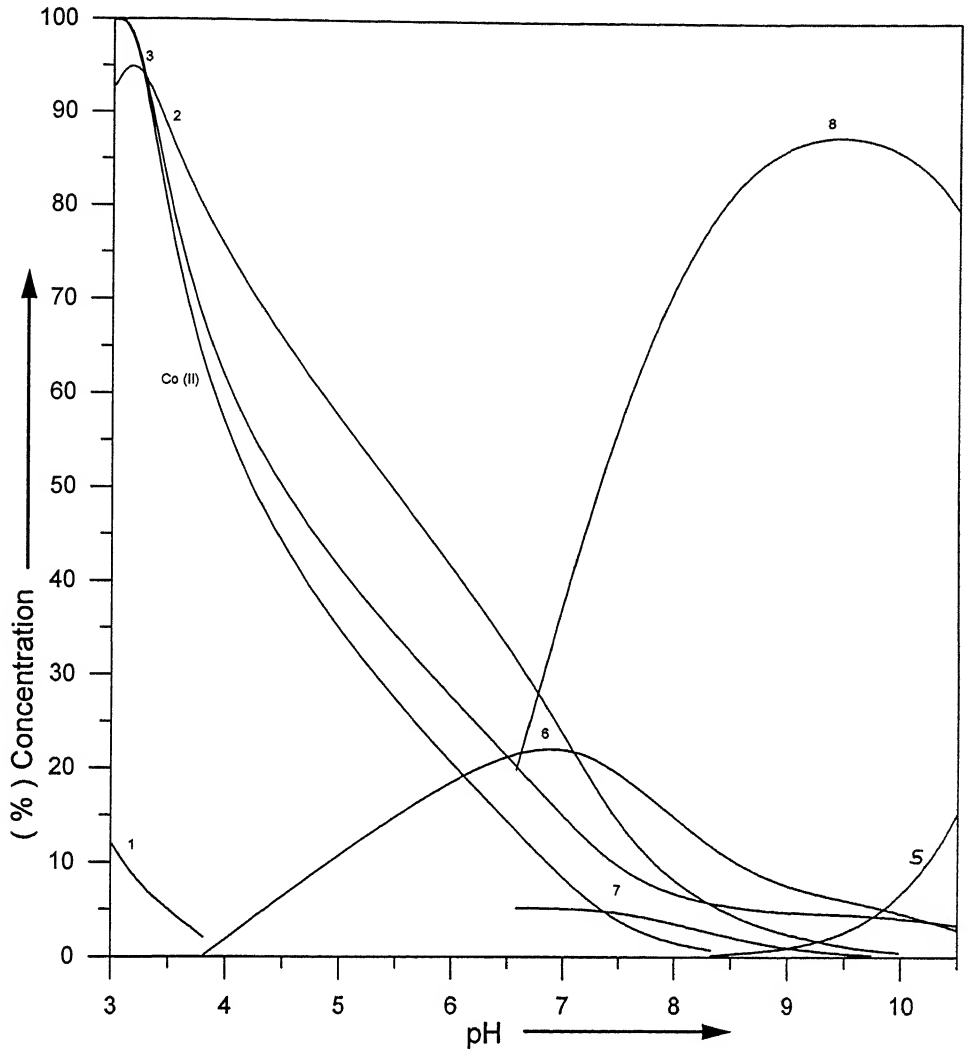



Fig.4.29- Distribution Curves of 1:1:1 Co(II)-Asparagine-Thymine system; (I) $AH_2$ (2) AH (3) BH (4) $Co(OH)^+$ (5) $Co(OH)_2$ (6) CoA (7) CoB (8) CoAB

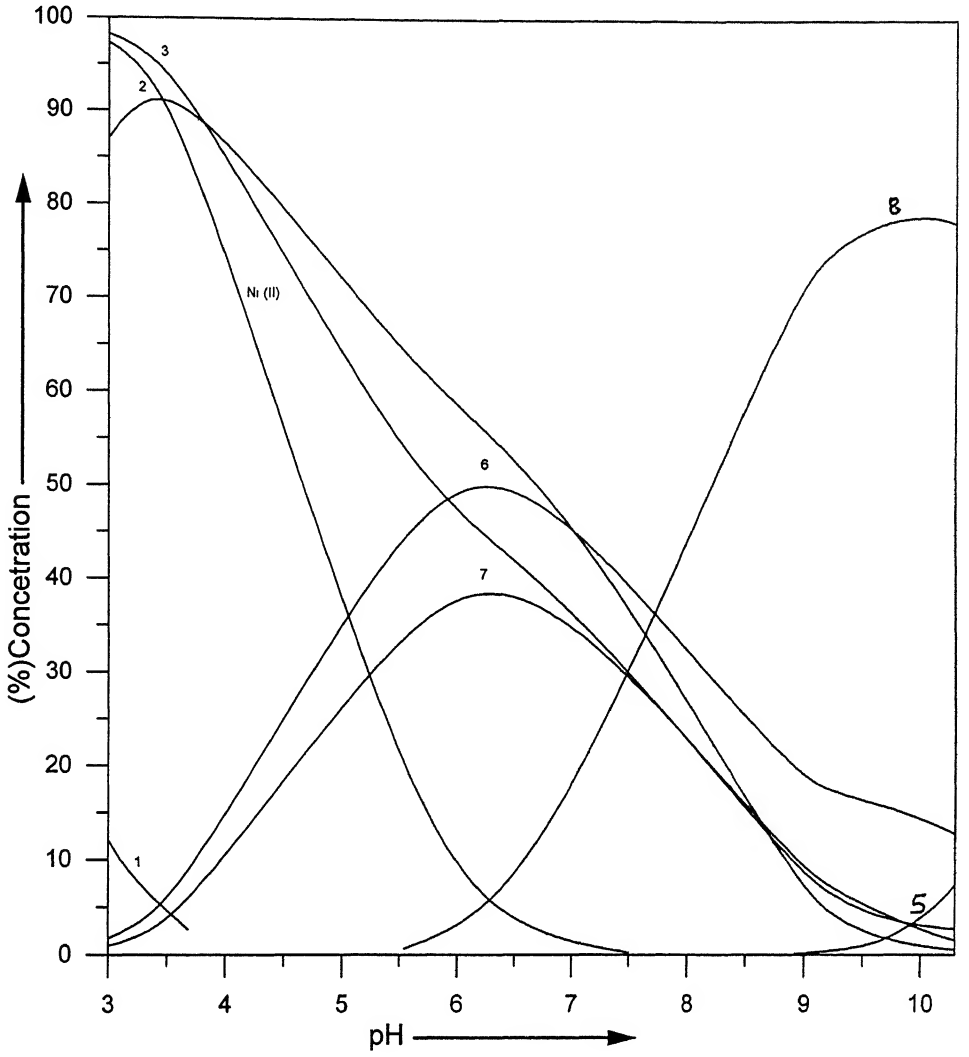



Fig.4.30- Distribution Curves of 1:1:1 Ni(II)-Asparagine-Thymine system; (I) $AH_2$ (2) AH (3) BH (4) $Ni(OH)^+$ (5) $Ni(OH)_2$ (6) NiA (7) NiB (8) NiAB

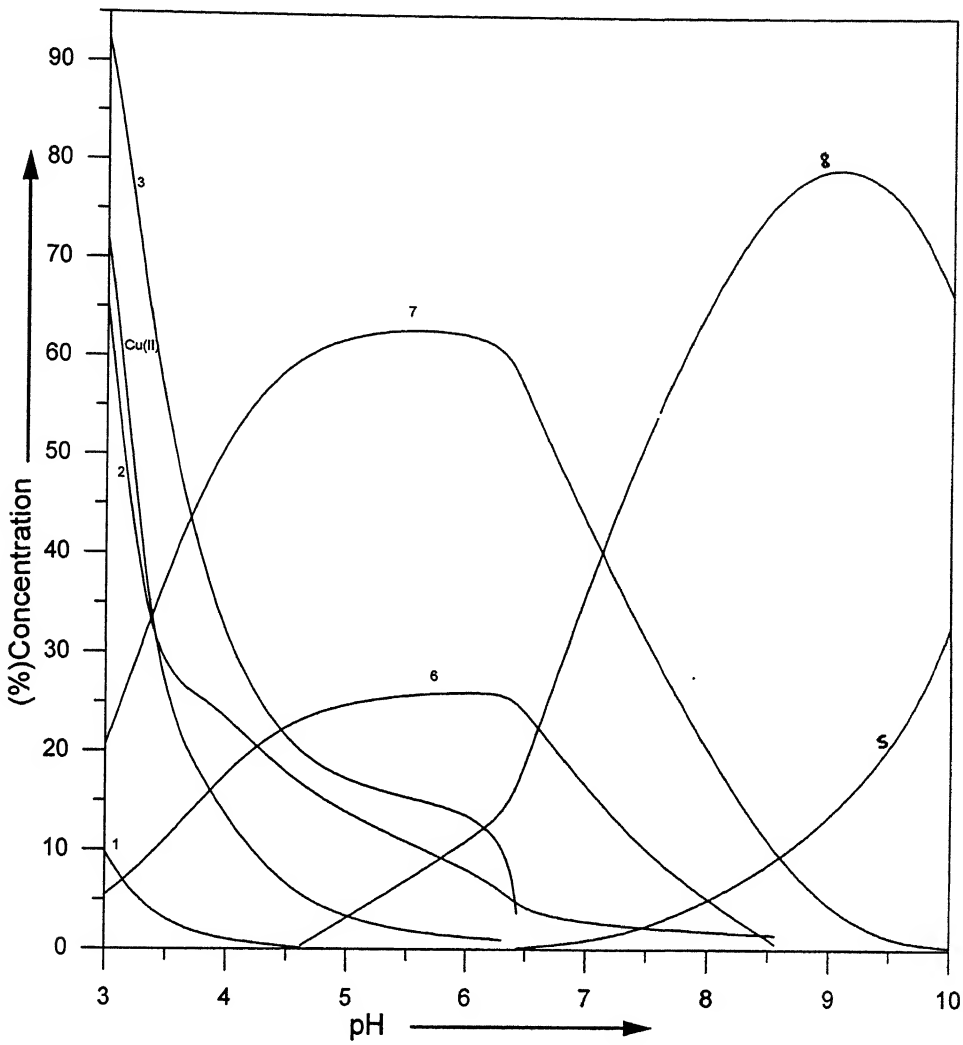



Fig.4.31- Distribution Curves of 1:1:1 Cu(II)-Asparagine-Thymine system; (I) $AH_2$ (2) AH (3) BH (4) $Cu(OH)^+$ (5) $Cu(OH)_2$ (6) CuA (7) CuB (8) CuAB

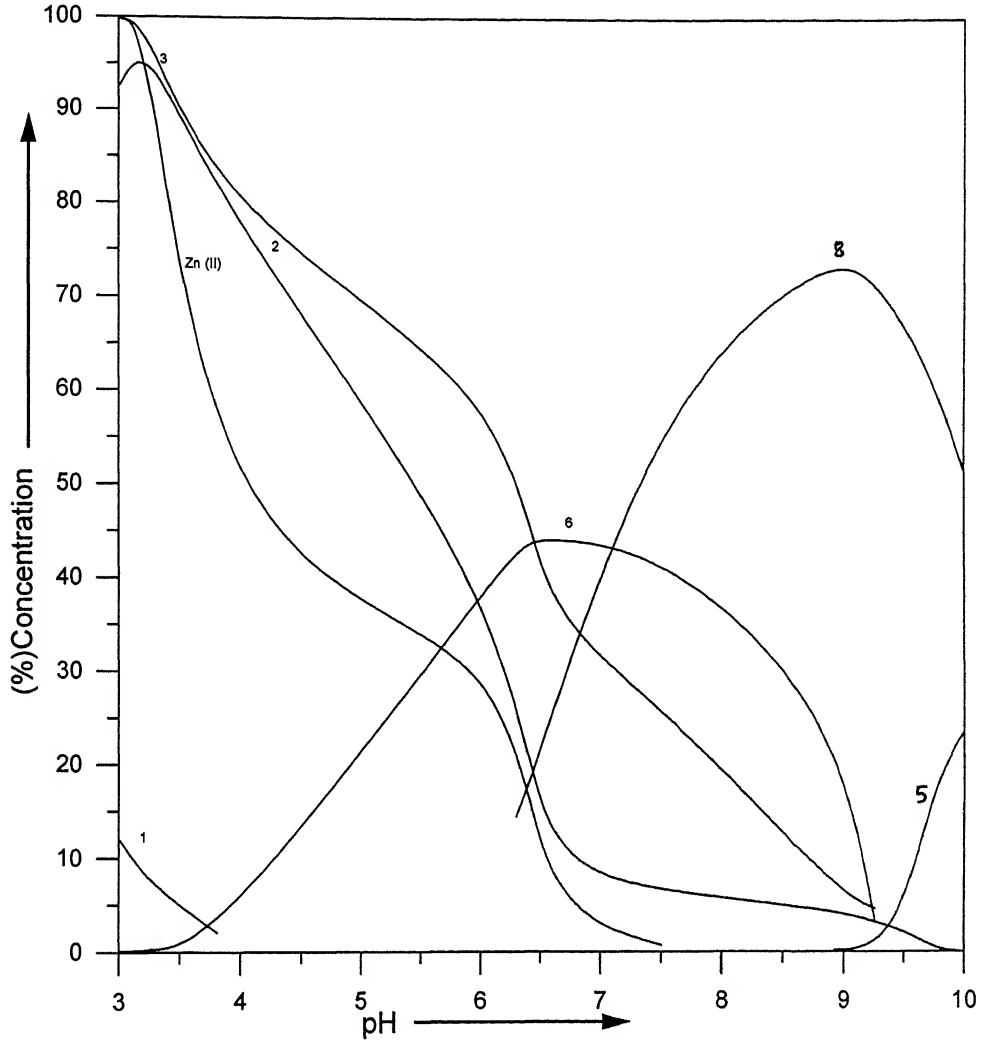



Fig.4.32-Distribution Curves of 1:1:1 Zn(II)-Asparagine-Thymine system; (I) $AH_2$ (2) AH (3) BH (4) $Zn(OH)^+$ (5) $Zn(OH)_2$ (6) ZnA (7) ZnB (8) ZnAB

## Quaternary Metal Chelates

***Titration curves-*** The following solution sets were prepared in aqueous medium, keeping molar ratio 1:1:1:1 and total volume 50 ml in each case.

***Solution A-*** 5ml $NaNO_3$(1.0M) + 5ml $HNO_3$ (0.02M) + 40ml $H_2O$

***Solution B-*** 5ml $NaNO_3$(1.0M) + 5ml $HNO_3$ (0.02M) + 5ml ligand (A/B) (0.01M) + 35ml $H_2O$

***Solution C-*** 5ml $NaNO_3$(1.0M) + 5ml $HNO_3$ (0.02M) + 5ml ligand A (0.01M) + 5ml $M_1$(II) (0.01M) + 30ml $H_2O$

***Solution D-*** 5ml $NaNO_3$(1.0M) + 5ml $HNO_3$ (0.02M) + 5ml ligand A (0.01M) + 5ml $M_1$(II) (0.01M) + 5ml ligand B (0.01M) + 25 ml $H_2O$

***Solution E-*** 5ml $NaNO_3$(1.0M) + 5ml $HNO_3$ (0.02M) + 5ml ligand A (0.01M) + 5ml $M_1$(II) (0.01M) + 5ml ligand B (0.01M) + 5ml $M_2$(II) (0.01M) + 20 ml $H_2O$

where A = L/ P/ V/A (L = Lysine, P = Proline, V = Valine, A = Asparagine)

B = U/T (U = Uracil, T = Thymine)

$M_1/M_2$ = Co/Ni/Cu/Zn

Procedure for the titration has already been described in the chapter III of the thesis. The pH titration curves are presented in the fig.(4.33-4.56).

A typical species distribution curves is shown in the fig.(4.57-4.80). In each case, attempts were made to fit a large number of different models to

the experimental data and the model quoted in the tables (4.18-4.42), gave indisputably the best statistical fit. It is therefore reasonable to claim that all the complexed species are actually present in the equilibrium mixture although there is uncertainty about the binary complex species.

## Cu(II)-Ni (II)-Lysine-Uracil (1:1:1:1) System

The system [Cu(II)-Ni(II)-Lysine-Uracil] are presented in fig.(4.33) and fig.(4.57) The metal titration curves are well separated from acid and ligand titration curves indicating the formation of metal complex in solution. The titration studies show that the curve E withdraws from the curve D at pH ~8.0 to point out the quaternary complexation.

The complex formation equilibria have been derived on the basis of speciation curves of the complexes occurs at different pH. Multinuclear complex i.e. quaternary complex species, protonated species; $AH_3$, $AH_2$, AH, BH, binary and ternary complex species CuAB exist in genuine concentration. The free metal ions exist in declining manner whereas, the metal hydroxo species are also present throughout the pH range.

The speciation curves clearly shows that the concentration of $AH_3$, $AH_2$, AH and BH species of both ligands are found to be in decreasing pattern with increase in pH within the range ~3.0-3.5, which indicates their involvement in complex formation.

The complexation equilibria of binary complexes are as follows:

$$[AH]^{2-} + Cu^{2+} \rightleftharpoons [Cu(II)\text{-}A]^{-} + H^{+}$$

$$[BH]^{-} + Cu^{2+} \rightleftharpoons [Cu(II)\text{-}BH]^{+}$$

$$[BH]^{-} + Ni^{2+} \rightleftharpoons [Ni(II)\text{-}BH]^{+}$$

Mixed ligand complex species [Cu(II)-A-B] and [Ni(II)-A-B] show their maximum concentration at pH ~9.8-10.0 attaining ≈10% and ≈30% respectively .

$$[Cu(II)\text{-}BH]^{+} + AH^{2-} \rightleftharpoons [Cu(II)\text{-}A\text{-}BH]^{2-} + H^{+}$$

$$[Ni(II)\text{-}BH]^{+} + AH^{2-} \rightleftharpoons [Ni(II)\text{-}A\text{-}BH]^{2-} + H^{+}$$

For quaternary system, the species distribution curve indicates the formation of heterobinuclear complex according to the following equilibria:

$$[AH]^{2-} + Cu^{2+} + [BH]^{-} + Ni^{2+} \rightleftharpoons [Cu(II)\text{-}Ni(II)\text{-}A\text{-}B]^{-} + 2H^{+}$$

The alternative equilibrium is also mentioned as follows:

$$[Cu(II)\text{-}A\text{-}BH]^{2-} + Ni^{2+} \rightleftharpoons [Cu(II)\text{-}Ni(II)\text{-}A\text{-}B]^{-} + H^{+}$$

It is clearly evident from the speciation curves that there is concomitant fall in the concentration of $Cu^{2+}$ and $Ni^{2+}$ aqueous ions with the increase in the concentration of quaternary complex species.

The concentration of quaternary complex is increasing gradually with gradual increase in pH and attains a maximum value ≈85% in the pH range ~6.8-8.5. The complexation starts from the very beginning of the titration, which shows the simultaneous process of complex formation.

The hydroxo species viz. $Ni(II)(OH)_2$ have been taken into consideration, as the buffer region corresponding to metal-ligand complex

formation equilibria are found to be overlapping with the hydrolytic equilibria of the $Ni^{2+}$(aq.) ions.

$$Ni^{2+} + 2H_2O \rightleftharpoons Ni(II)(OH)_2 + 2H^+$$

## Cu(II)-Zn(II)-Lysine-Uracil (1:1:1:1) System

Titration curves for [Cu(II)-Zn(II)-Lysine-Uracil] system are presented in fig.(4.34) and Speciation curves are represented in fig.(4.58). By pH titration curves it is clear that the curve E set apart from curve D at pH ~7.8 consumes ~1.5ml, which indicates the complex formation.

Multimetal-multiligand complexation equilibria have been illustrated on the basis of the concentration of the complexes formed in the system. The protonated species $AH_3$, $AH_2$, AH, BH, binary, ternary free metal ions and hydroxo species has been detected throughout the pH range.

The species distribution curves clearly show that the concentration of $AH_3$, $AH_2$, AH and BH species of both ligands are found to be decreasing with increase pH in the range ~3.0-7.5, whereas the species AH first increases with increase in pH ~3.0-3.5, and then decreases in the pH range ~3.5-7.0.

In addition to protonated ligand and hydroxide species, the curves indicate the formation of binary complexes CuA and ZnB at pH ~3.5 and ~7.7 respectively whereas CuB and ZnA species do not exist in the system.

$$[AH]^{2-} + Cu^{2+} \rightleftharpoons [Cu(II)\text{-}A]^- + H^+$$

$$[BH]^- + Zn^{2+} \rightleftharpoons [Zn(II)\text{-}BH]^+$$

Ternary complexes with $Cu^{2+}$(aq.) and $Zn^{2+}$(aq.) is found to be remarkable species in the pH range ~7.0-10.0.

$$[Cu(II)\text{-}A]^{-} + [BH]^{-} \rightleftharpoons [Cu(II)\text{-}A\text{-}BH]^{2-}$$

The alternative form of equilibrium is as follows:

$$[Zn(II)\text{-}BH]^{+} + [AH]^{2-} \rightleftharpoons [Zn(II)\text{-}A\text{-}BH]^{2-} + H^{+}$$

Simultaneous formation of heterobinuclear complex may be described by the speciation curves as follows:

$$Cu^{2+} + [AH]^{2-} + [BH]^{-} + Zn^{2+} \rightleftharpoons [Cu(II)\text{-}Zn(II)\text{-}A\text{-}B]^{-} + 2H^{+}$$

The another form of equilibrium can be assumed as follows:

$$[Cu(II)\text{-}A\text{-}BH]^{2-} + Zn^{2+} \rightleftharpoons [Cu(II)\text{-}Zn(II)\text{-}A\text{-}B]^{-} + 2H^{+}$$

Species distribution curves clearly show that there is continuous decline in the concentration of $Cu^{2+}$ and $Zn^{2+}$ aqueous ions with the incline in the concentration of quaternary complex species attaining a maximum value $\approx$87% at pH ~7.7. The complexation starts from the very beginning of the titration, which indicates the simultaneous process of complex formation.

The metal hydroxo species viz. $Cu(II)(OH)^{+}$ and $Zn(II)(OH)^{+}$ exist at higher pH, involving the following equilibrium:

$$Cu^{2+} + H_2O \rightleftharpoons Cu(II)(OH)^{+} + H^{+}$$

$$Zn^{2+} + H_2O \rightleftharpoons Zn(II)(OH)^{+} + H^{+}$$

The dissociation of quaternary complex beyond pH ~7.7, may be explained probably due to the formation of metal hydroxo species.

## Cu(II)-Co(II)-Lysine-Uracil (1:1:1:1) System

pH titration curves and Species distribution curves of [Cu(II)-Co(II)-Lysine-Uracil] system are presented in fig.(4.35) and fig.(4.59) respectively. The titration curves clearly indicate that the deflection of curve E (quaternary) form curve D (ternary), formation of multinuclear complex at pH ~7.8 consumes ≈1.5ml alkali. In present system, multimetal-mutliligand complex i.e. quaternary complex species, protonated species $AH_3$, $AH_2$, AH, BH, binary and the ternary complex species, exist in sufficient concentration. The hydroxo species and free metal ions are also present throughout the entire pH range.

Formation curves clearly indicate that the concentration of $AH_3$, $AH_2$ and BH species of both ligands are found to be decreasing with increase in pH in the range ~3.0- 7.5 whereas species AH increases with increase in pH and attains maximum concentration ≈42% at pH ~3.5, further decreasing in the pH range ~3.5-7.6, which shows their involvement in the complex formation.

Binary complexation starts at lower pH. From the distribution profiles, it appears that the binary complexes are formed according to the equilibria:

$$[AH]^{2-} + Cu^{2+} \rightleftharpoons [Cu(II)\text{-}A]^{-} + H^{+}$$

$$[BH]^{-} + Cu^{2+} \rightleftharpoons [Cu(II)\text{-}BH]^{+}$$

$$[BH]^{-} + Co^{2+} \rightleftharpoons [Co(II)\text{-}BH]^{+}$$

The concentration of binary complexes CuA and CuB are maximum at pH ~4.5. The species [Co(II)-BH] attains maximum value ≈25% at higher pH ~9.1, while [Co(II)-A] complex species does not exist throughout entire pH range. The concentrations of all binary species are decreasing with further increase in pH, probably due to the formation of ternary and quaternary complexes.

Mixed ligand complexes with $Cu^{2+}$(aq.) and $Co^{2+}$(aq.) are found to be the remarkable species in the pH range ~6.5-10.0, as follows:

$$Cu^{2+} + [AH]^{2-} + [BH]^{-} \rightleftharpoons [Cu(II)\text{-}A\text{-}BH]^{2-} + H^{+}$$

$$Co^{2+} + [AH]^{2-} + [BH]^{-} \rightleftharpoons [Co(II)\text{-}A\text{-}BH]^{2-} + H^{+}$$

The alternative equilibria may also be indicated as follows:

$$[Cu(II)\text{-}BH]^{+} + [AH]^{2-} \rightleftharpoons [Cu(II)\text{-}A\text{-}BH]^{2-} + H^{+}$$

$$[Cu(II)\text{-}A]^{-} + [BH]^{-} \rightleftharpoons [Cu(II)\text{-}A\text{-}BH]^{2-}$$

It is clearly evident from the distribution curves that the [Cu(II)-A-BH] is the major ternary species attaining ≈40% at higher pH ~10.0 whereas [Co (II)-A-BH] does not exist in the present system.

For quaternary system, the speciation curves indicate the formation of heterobinuclear complex according to the following equilibria:

$$[AH]^{2-} + Cu^{2+} + [BH]^{-} + Co^{2+} \rightleftharpoons [Cu(II)\text{-}Co(II)\text{-}A\text{-}B]^{-} + 2H^{+}$$

The another form of multinuclear equilibrium can be written as :

$$[Cu\ (II)\text{-}A\text{-}BH\ ]^{2-} + Co^{2+} \rightleftharpoons [Cu(II)\text{-}Co(II)\text{-}A\text{-}B]^{-} + H^{+}$$

Formation curves show that there is concomitant decline in the concentration of $Cu^{2+}$ and $Co^{2+}$ aqueous ions with the incline in the concentration of quaternary complex species. The concentration of multinuclear complex is increasing gradually with the gradual increase in pH and attains a maximum value $\approx$76% in the pH range ~7.5-8.5. The complexation starts from the very beginning of the titration, which shows the simultaneous process of complex formation.

Metal hydroxo species viz. $Co(II)(OH)^{+}$, $Co(II)(OH)_2$ exist in the pH range ~8.0-10.0 involving the following equilibrium:

$$Co^{2+} + H_2O \rightleftharpoons Co(II)(OH)^{+} + H^{+}$$

$$Co^{2+} + 2H_2O \rightleftharpoons Co(II)(OH)_2 + 2H^{+}$$

## Ni(II)-Zn(II)-Lysine-Uracil (1:1:1:1) System

Fig.(4.36) and fig.(4.60) represent titration curves and speciation curves of the present quaternary system respectively. Potentiometric curves clearly indicate that the complexation starts at pH ~8.0. In this multimetal-multiligand system following species are assumed to exist viz. $AH_3$, $AH_2$, AH, BH, $Ni(OH)^{+}$, $Ni(OH)_2$, $Zn(OH)^{+}$, $Zn(OH)_2$, [Ni(II)-Lysine], [Ni(II)-

Uracil], [Zn(II)-Lysine], [Zn(II)-Uracil], [Ni(II)-Lysine-Uracil], [Zn(II)-Lysine-Uracil] and [Ni(II)-Zn(II)-Lysine-Uracil].

The protonated ligand species of both the ligands and free metal ions $Ni^{2+}$(aq.) and $Zn^{2+}$(aq.) have been found to follow a declining pattern of their concentration with rise in pH .The concentration of $AH_3$, $AH_2$, AH and BH species of both the ligands are found to be decreasing with increase in the pH range ~3.0-7.0, which shows their involvement in the complex formation.

The binary complexes show their remarkable presence according to the following equilibria:

$$[AH]^{2-} + Ni^{2+} \rightleftharpoons [Ni(II)\text{-}A]^{-} + H^{+}$$

$$[BH]^{-} + Ni^{2+} \rightleftharpoons [Ni(II)\text{-}BH]^{+}$$

Binary complexes CuA and CuB shows their existence in the present system. Their formation start right from the beginning of the titration and after a gradual incline, their concentration becomes maximum at higher pH ~10.0 and ~9.0 respectively. At still higher pH, these follow a declining pattern of their concentrations.

Mixed ligand complexes with $Ni^{2+}$(aq.) and $Zn^{2+}$(aq.) are found to be remarkable species in the pH range ~8.3-10.5 as follows:

$$Ni^{2+} + [AH]^{2-} + [BH]^{-} \rightleftharpoons [Ni(II)\text{-}A\text{-}BH]^{2-} + H^{+}$$

$$[Ni(II)\text{-}BH]^{+} + [AH]^{-} \rightleftharpoons [Ni(II)\text{-}A\text{-}BH]^{2-} + H^{+}$$

For quaternary system, the species distribution curve indicates the formation of heterobinuclear complex according to the following equilibria:

$Ni^{2+} + [AH]^{2-} + Zn^{2+} + [BH]^{-} \rightleftharpoons [Ni(II)\text{-}Zn(II)\text{-}A\text{-}B]^{-} + 2H^{+}$

There is concomitant decline in the concentrations of $Ni^{2+}$ and $Zn^{2+}$ aqueous ions with the incline in the concentration of quaternary complex species. The multinuclear complex species are predominant species in the present system.

The metal hydroxo species are formed in the system which indicates the dissociation of quaternary species,

$Ni^{2+} + 2H_2O \rightleftharpoons Ni(II)(OH)_2 + 2H^{+}$

$Zn^{2+} + 2H_2O \rightleftharpoons Zn(II)(OH)_2 + 2H^{+}$

## Ni(II)-Co(II)-Lysine-Uracil -(1:1:1:1) System

Titration curves of [Ni(II)-Co(II)-Lysine-Uracil] system are presented in fig.(4.37) and Speciation curves are represented in fig.(4.61). Following species are assumed to prevail in the present system: $AH_3$, $AH_2$, AH, BH, $M_1(OH)$, $M_1(OH)_2$, $M_2(OH)$, $M_2(OH)_2$, $M_1A$, $M_1B$, $M_2B$, $M_2B$, $M_1AB$ and $M_1$ $M_2$ AB.All the protonated ligand species are found to exist in the decreasing order of their concentrations. The free metal ions are also existing in the system in a declining trend as usual.

It is clearly evident from the speciation curves that the concentration of $AH_3$, $AH_2$, AH and BH species of both the ligands are found to be decreasing with increase in pH in the range ~3.0-6.0, indicating the metal ligand complex formation.

Formation of binary complexes [Ni(II)-Lysine], [Co(II)-Lysine] and [Co(II)-Uracil] can be written as following :

$$[AH_2]^- + Ni^{2+} \rightleftharpoons [Ni(II)\text{-}A]^- + 2H^+$$

$$[AH]^{2-} + Co^{2+} \rightleftharpoons [Co(II)\text{-}A]^- + H^+$$

$$[BH]^- + Co^{2+} \rightleftharpoons [Co(II)\text{-}BH]^+$$

The formation of complex [Ni(II)-A] and [Co(II)-A] binary species starts in the beginning of titration while the $[Co(II)\text{-}BH]^+$ are formed at higher pH. Speciation curves of binary (1:1) system indicate the formation of binary complexes in the pH range ~4.0-10.0. At higher pH region there is gradual decline in the concentration of [Ni(II)-A] , [Co(II)-A] and $[Co(II)\text{-}BH]^+$ due to the appearance of hydroxo species. The ternary complex species NiAB and CoAB shows their remarkable presence ≈30% and ≈25%, respectively, there after their concentration decreases due to the appearance of hydroxo species. Fall in the concentration of binary complex species with the concomitant rise in the concentration of mixed ligand complexes is in the pH range ~8.0-10.2 is governed according to the equilibria:

$$[AH]^{2-} + Ni^{2+} + [BH]^- \rightleftharpoons [Ni(II)\text{-}A\text{-}BH]^{2-} + H^+$$

The alternative equilibrium of mixed ligand complexes is as follows,

$$[Co(II)\text{-}BH]^+ + [AH]^{2-} \rightleftharpoons [Co(II)\text{-}A\text{-}BH]^{2-} + H^+$$

For quaternary system, the species distribution curve indicates the formation of heterobinuclear complexes according to the following equilibria:

$$Ni^{2+} + [AH]^{2-} + Co^{2+} + [BH]^{-} \rightleftharpoons [Ni(II)\text{-}Co(II)\text{-}A\text{-}B]^{-} + 2H^{+}$$

The another equilibria are also indicated as follows:

$$[Ni(II)\text{-}A\text{-}BH]^{2-} + Co^{2+} \rightleftharpoons [Ni(II)\text{-}Co(II)\text{-}A\text{-}B]^{-} + H^{+}$$

$$[Co(II)\text{-}A\text{-}BH]^{2-} + Ni^{2+} \rightleftharpoons [Co(II)\text{-}Ni(II)\text{-}A\text{-}B]^{-} + H^{+}$$

Formation curves clearly show that there is concomitant decline in the concentration of $Ni^{2+}$ and $Co^{2+}$ aqueous ions with the incline in the concentration of quaternary complex species. The concentration of multimetal-multiligand complex is increasing gradually with the gradual increase in pH and attains a maximum value $\approx$78% at pH ~8.2. The complexation starts at pH ~3.7, which shows the simultaneous process of complex formation.

Metal hydroxo species viz. $Ni(II)(OH)_2$ , $Co(II)(OH)^{+}$ and $Co(II)(OH)_2$ exist in the pH range ~6.5-10.2 involving the following equilibrium :

$$Ni^{2+} + 2H_2O \rightleftharpoons Ni(II)(OH)_2 + 2H^{+}$$

$$Co^{2+} + H_2O \rightleftharpoons Co(II)(OH)^{+} + H^{+}$$

$$Co^{2+} + 2H_2O \rightleftharpoons Co(II)(OH)_2 + 2H^{+}$$

## Zn(II)-Co(II)-Lysine-Uracil (1:1:1:1) System

pH tritration curve and Formation curve for [Zn(II)-Co(II)-Lysine-Uracil] system are presented in fig.(4.38) and fig.(4.62) respectively. Multimetal-multiligand complexation equilibrium involves i.e. quaternary complex species $AH_3$, $AH_2$, AH, BH, binary and ternary complexes in good concentration. The free metal ions and hydroxo species are also present throughout the pH range.

It is clear form the species distribution curves shows that the concentration of $AH_3$, $AH_2$, AH and BH species of both the ligands are found to be decreasing with increase in pH within the range ~3.0-7.5, which indicates their involvement in the complex formation.

The concentration of binary complexes ZnB, CoA and CoB are maximum in the pH range ~6.5-9.5, while ZnA complex species does not exist in the system. The formation of binary complexes occurs according to the following equilibria:

$$Zn^{2+} + [BH]^{-} \rightleftharpoons [Zn(II)\text{-}BH]^{+}$$

$$Co^{2+} + [AH]^{-} \rightleftharpoons [Co(II)\text{-}A] + H^{+}$$

$$Co^{2+} + [BH]^{-} \rightleftharpoons [Co(II)\text{-}BH]^{+}$$

Mixed ligand complexes with $Zn^{2+}$(aq.) and $Co^{2+}$(aq.) are found to be remarkable species in the pH range ~8.0-10.0 as follows:

$$[AH]^{2-} + Zn^{2+} + [BH]^{-} \rightleftharpoons [Zn(II)\text{-}A\text{-}BH]^{2-} + H^{+}$$

The alternative equilibrium is also indicated as follows,

$$[Co(II)\text{-}BH]^{+} + [AH]^{2-} \rightleftharpoons [Co(II)\text{-}A\text{-}BH]^{2-} + H^{+}$$

For the present heterobinuclear system the formation of quaternary complex may be according to the following equilibria:

$$[AH]^{2-} + Zn^{2+} + [BH]^{-} + Co^{2+} \rightleftharpoons [Zn(II)\text{-}Co(II)\text{-}A\text{-}B]^{-} + 2H^{+}$$

Besides, the simultaneous complex formation, the another form of equilibrium is shown as follows:

$$[Co(II)\text{-}A\text{-}BH]^{2-} + Zn^{2+} \rightleftharpoons [Zn(II)\text{-}Co(II)\text{-}A\text{-}B]^{-} + H^{+}$$

This is the stepwise process of complexation.

It is clear from the speciation curves that there is decrease in the concentration of $Zn^{2+}$ and $Co^{2+}$ aqueous ions with the incline in the concentration of quaternary complex species. The concentration of quaternary complex is increasing gradually with the gradual increase in the pH and attains a maximum value $\approx$74% at pH ~7.7.

The equilibrium of metal hydroxo species can be written as:

$$Zn^{2+} + H_2O \rightleftharpoons Zn(II)(OH)^{+} + H^{+}$$

$$Zn^{2+} + 2H_2O \rightleftharpoons Zn(II)(OH)_2 + 2H^{+}$$

$$Co^{2+} + 2H_2O \rightleftharpoons Co(II)(OH)_2 + 2H^{+}$$

## Cu(II)-Ni(II)-Proline-Uracil ( 1:1:1:1) System

pH titration curves and Species distribution curves for [Cu(II)-Ni(II)-Proline] system are presented in fig.(4.39) and fig.(4.63) respectively. Following species are assumed to occur in the present multinuclear system: Protonated species $AH_2$, AH, BH, binary, ternary CuAB, NiAB and quaternary [Cu(II)-Ni(II)-A-B] complex species exist in its maximum abundance.

The speciation curves clearly shows that the concentration of $AH_2$, AH and BH species of both ligands are found to be decreasing with increase in the pH range ~3.0-5.0, which indicates their involvement in complex formation.

Speciation curves of binary complexes CuA and NiB systems indicates the formation of binary complexes at pH ~4.2 and ~9.5 respectively, whereas the CuB and NiA do not present in the system.

From the distribution profiles, it appears that the binary complexes are formed according to the following equilibria:

$$[AH]^- + Cu^{2+} \rightleftharpoons [Cu(II)\text{-}A] + H^+$$

$$[BH]^- + Ni^{2+} \rightleftharpoons [Ni(II)\text{-}BH]^+ + H^+$$

Mixed ligand CuAB and NiAB complex species shows maximum presence at pH ~10.5, ≈15% and ≈70% respectively, thereafter its concentration decreases due to the appearance of hydroxo species.

Mixed ligand complexation equilibrium has been assumed as follows:

$$[AH]^- + Cu^{2+} + [BH]^- \rightleftharpoons [Cu(II)\text{-}A\text{-}BH]^- + H^+$$

$$[Ni(II)\text{-}BH]^{+} + [AH]^{-} \rightleftharpoons [Ni(II)\text{-}A\text{-}BH]^{-} + H^{+}$$

It is clearly evident from the speciation curves that there is concomitant decrease in the concentration of $Cu^{2+}$ and $Ni^{2+}$ aqueous ions with the increase in the concentration of quaternary complex species. The concentration of quaternary complex is increasing gradually with gradual increase in pH and attains a maximum value $\approx$95% in the pH range ~3.0-10.5. The complexation starts from the very beginning of the titration ~3.1, which shows the simultaneous process of complex formation.

For quaternary system, the species distribution curve indicates the formation of heterobinuclear complex according to the following equilibria:

$$[AH]^{-} + Cu^{2+} + [BH]^{-} + Ni^{2+} \rightleftharpoons [Cu(II)\text{-}Ni(II)\text{-}A\text{-}B] + 2H^{+}$$

The alternative equilibrium is also indicated as follows:

$$[Cu(II)\text{-}A\text{-}BH]^{-} + Ni^{2+} \rightleftharpoons [Cu(II)\text{-}Ni(II)\text{-}A\text{-}B] + H^{+}$$

$$[Ni(II)\text{-}A\text{-}BH]^{-} + Cu^{2+} \rightleftharpoons [Ni(II)\text{-}Cu(II)\text{-}A\text{-}B] + H^{+}$$

Formation of hydroxo species viz.-$Cu(II)(OH)_2$ and $Ni(II)(OH)^{+}$ have been taken into consideration, as the buffer regions corresponding to metal-ligand complex formation equilibria are found to be overlapping with the hydrolytic equilibria of $M^{2+}$(aq.) ions.

$$Cu^{2+} + 2H_2O \rightleftharpoons Cu(II)(OH)_2 + 2H^{+}$$

$$Ni^{2+} + H_2O \rightleftharpoons Ni(II)(OH)^{+} + H^{+}$$

## Cu(II)-Zn(II)-Proline-Uracil (1:1:1:1) System

Titration curves and Formation curves for [Cu(II)-Zn(II)-Proline-Uracil] system presented in fig.(4.40) and fig.(4.64) respectively. By pH titration curves, it is clearly shown that the curve E set apart from curve D at pH ~7.5, which indicates the complex formation.

On the basis of speciation curves of multimetal-multiligand complex formation eqilibrium, protonated species; $AH_2$, AH, BH, binary and ternary complex species CuAB exist in genuine concentration. The metal ions also exist in declining manner in the present system, whereas the metal hydroxo species are present in the higher pH region.

The speciation curve clearly shows that the concentration of $AH_2$, AH and BH of both the ligands are found to be decreasing with increase in pH, which indicates their involvement in the complex formation.

The concentration of binary CuA and ZnB are maximum in the pH range ~3.0-9.0, whereas, CuB and ZnB are absent in the system. The maximum percent of CuA and ZnB are $\approx$15% and $\approx$10% respectively. The formation equilibria of binary complexes are assumed as follows:

$$[AH]^{-} + Cu^{2+} \rightleftharpoons [Cu(II)\text{-}A] + H^{+}$$

$$[BH]^{-} + Zn^{2+} \rightleftharpoons [Zn(II)\text{-}BH]^{+}$$

Mixed ligand complexes CuAB and NiAB both exist in the system. The concentration of binary complexes gradually decline with increase in the pH, which indicates the formation of mixed ligand complexes .The complexation equilibria of ternary complexes as follows:

$$[Zn(II)\text{-}BH]^{+} + [AH]^{-} \rightleftharpoons [Zn(II)\text{-}A\text{-}BH]^{-} + H^{+}$$

Further, the simultaneous formation equilibria is explained as follows:

$$[AH]^{-} + Cu^{2+} + [BH]^{-} \rightleftharpoons [Cu(II)\text{-}A\text{-}BH]^{-} + H^{+}$$

The concentration of free metal ions $Cu^{2+}$(aq.) and $Zn^{2+}$(aq.) show concomitant decline with increase in pH, which is probably due to its involvement in the formation of quaternary complex species CuZnAB.

For multinuclear system, the species distribution curve indicates the formation of heterobinuclear complex according to the following equilibrium:

$$[AH]^{-} + Cu^{2+} + [BH]^{-} + Zn^{2+} \rightleftharpoons [Cu(II)\text{-}Zn(II)\text{-}A\text{-}B] + 2H^{+}$$

The alternative equilibrium is also indicated as follows:

$$[Cu(II)\text{-}A\text{-}BH]^{-} + Zn^{2+} \rightleftharpoons [Cu(II)\text{-}Zn(II)\text{-}A\text{-}B] + H^{+}$$

$$[Zn(II)\text{-}A\text{-}BH]^{-} + Cu^{2+} \rightleftharpoons [Zn(II)\text{-}Cu(II)\text{-}A\text{-}B] + H^{+}$$

Metal hydroxo species viz. $Cu(II)(OH)_2$ exist at higher pH, involving the following equilibrium:

$$Cu^{2+} + 2H_2O \rightleftharpoons [Cu(II)(OH)_2] + 2H^+$$

## Cu(II)-Co(II)-Proline-Uracil (1:1:1:1) System

Fig.(4.41) and fig.(4.65) represent Titration curves and Speciation curves in the present quaternary system respectively. Following species were assumed to exist in the present system: $AH_2$, AH, BH, $Cu(OH)^+$, $Cu(OH)_2$, $Co(OH)^+$, $Co(OH)_2$, [Cu(II)-Proline], [Cu(II)-Uracil], [Co(II)-Proline], [Co(II)-Uracil], [Cu(II)-Proline-Uracil], [Co(II)-Proline-Uracil] and [Cu(II)-Co(II)-Proline-Uracil].

Among the species assumed, the protonated ligand species of both the ligands and free metal ions $Cu^{2+}$(aq.) and $Co^{2+}$(aq.) have been found to follow a declining pattern in their concentration with rise in pH. The coordination of both the metal ions with the protonated ligand species may be concluded on the basis of appearance and gradual increase in the concentration of binary, ternary and quaternary complex species.

These binary complexes show their remarkable presence according to the following equilibria:

$$[AH_2] + Cu^{2+} \rightleftharpoons [Cu(II)\text{-}A] + 2H^+$$

$$[AH]^- + Co^{2+} \rightleftharpoons [Co(II)\text{-}A] + H^+$$

$$[BH]^- + Co^{2+} \rightleftharpoons [Co(II)\text{-}BH]^+$$

Binary complex [Cu(II)-A] shows its existence in the low pH region. Its formation starts right from the beginning of the titration and after a gradual incline, its concentration becomes maximum at pH ~4.5, being

≈19% at pH > 4.5, there is a gradual fall in its concentration reactivity upto negligible amount at pH >8.5 .

On the other hand, $Co^{2+}$ (aq.) is found to undergo complexation at higher pH region. Both the binary complex species of $Co^{2+}$(aq.) with the ligands appear at pH > 6.0. Rise in the concentration of CoA and CoB species continues up to pH ~9.0, their concentration being ≈15% and ≈10% respectively. At still higher pH, these follow a declining pattern of their concentration.

It is clearly evident from the speciation curves that the two types of ternary complex species have been examined in the present system [Cu(II)-A-BH]$^-$ and [Co(II)-A-BH]$^-$. It may be noticed that the ternary complex with primary metal ion shows its existence right from the beginning of the titration. Hence, its simultaneous formation may be explained as follows:

$$[AH]^- + Cu^{2+} + [BH]^- \rightleftharpoons [Cu(II)\text{-}A\text{-}BH]^- + H^+$$

Further the formation of [Co(II)-A-BH]$^-$ complex may be stepwise as its appearance starts from the pH ~7.8. The stepwise formation may be shown as:

$$[Co(II)\text{-}A] + [BH]^- \rightleftharpoons [Co(II)\text{-}A\text{-}BH]^-$$

The quaternary complex species is the predominant species in the present system. The coordination of $Cu^{2+}$ (aq.) and $Co^{2+}$(aq.) metal ion with the Proline and Uracil ligands may be explained on the basis of simultaneous process of complex formation. The following equilibrium has been proposed:

$$[AH]^- + Cu^{2+} + [BH]^- + Co^{2+} \rightleftharpoons [Cu(II)\text{-}Co(II)\text{-}A\text{-}B] + 2H^+$$

Alternative equilibrium is also indicated as follows:

$$[Cu(II)\text{-}A\text{-}BH]^- + Co^{2+} \rightleftharpoons [Cu(II)\text{-}Co(II)\text{-}A\text{-}B] + H^+$$

$$[Co(II)\text{-}A\text{-}BH]^- + Cu^{2+} \rightleftharpoons [Co(II)\text{-}Cu(II)\text{-}A\text{-}B] + H^+$$

It is clear from the species distribution curve diagram fig.(4.65) that there is gradual rise in the concentration multimetal-multiligand complex with the progressive addition of alkali. Maximum concentration of the complex is ≈70% at pH ~7.0. Its concentration thereafter follows a declining pattern as the metal-ligand formation equilibrium has been found to be overlapping with the hydrolytic equilibrium of $Cu^{2+}$(aq.) metal ion :

$$Cu^{2+} + 2H_2O \rightleftharpoons Cu(II)(OH)_2 + 2H^+$$

The concentration of $Cu(II)(OH)_2$ is approximately 35% at pH 10.0 and of the quaternary complex being minimum at the same pH .

## Ni(II)-Zn(II)-Proline-Uracil -( 1:1:1:1) System

Fig.(4.42) and fig.(4.66) represents Titration curves and Distribution curves respectively, of the present multinuclear systems represents $AH_2$,

$[AH]^-$, $[BH]^-$, $Ni(OH)^+$, $Ni(OH)_2$, $Zn(OH)^+$, $Zn(OH)_2$, [Ni(II)-Proline], [Ni(II)-Uracil], [Zn(II)-Proline], [Zn(II)-Uracil], [Ni(II)-Proline-Uracil], [Zn(II)-Proline-Uracil], [Ni(II)-Zn(II)-Proline-Uracil] are the species present in this system.

Multimetal-multiligand complexation equilibrium involves quaternary complex species, protonated species; $AH_2$, AH, BH, binary and ternary complex species are in good concentration. The coordination of both the protonated ligands with metal ions may be concluded on the basis of appearance and gradual increase in the concentration of binary, ternary and quaternary complex species.

Formation curves clearly indicate that the concentration of $AH_2$ and BH species of both the ligands are found to decreases with increase in the pH range ~ 3.2-6.0, whereas the species BH decreases in the pH range ~3.7-8.0, which shows their involvement in the complex formation. The concentration of binary complexes NiA, NiB and ZnA are maximum at pH range ~6.0-9.3, whereas the species ZnB is absent in the system. The binary complexes show their remarkable presence according to the following equlibria:

$$[AH_2] + Ni^{2+} \rightleftharpoons [Ni(II)\text{-}A] + 2H^+$$

$$[AH]^- + Ni^{2+} \rightleftharpoons [Ni(II)\text{-}A] + H^+$$

$$[BH]^- + Zn^{2+} \rightleftharpoons [Zn(II)\text{-}BH]^+$$

Mixed ligand complex with $Ni^{2+}$ (aq.) and $Zn^{2+}$(aq.) is also predominant in the system. The mixed chelates equilibrium has been examined in the present system as follows:

$$[AH_2] + Ni^{2+} + [BH]^- \rightleftharpoons [Ni(II)\text{-}A\text{-}BH]^- + 2H^+$$

$$[Zn(II)\text{-}BH]^+ + [AH]^- \rightleftharpoons [Zn(II)\text{-}A\text{-}BH]^- + H^+$$

For quaternary system, the distribution curve indicates the formation of heterobinuclear complex species according to the following equilibrium:

$$[AH]^- + Ni^{2+} + [BH]^- + Zn^{2+} \rightleftharpoons [Ni(II)\text{-}Zn(II)\text{-}A\text{-}B] + 2H^+$$

Speciation curves clearly show that there is continuous decrease in the concentration of $Ni^{2+}$ and $Zn^{2+}$ aqueous ions with increase in the concentration of quaternary complex species. The concentration of quaternary complex is increasing gradually with gradual increase in pH and attains a maximum value $\approx$70% at pH ~9.3. The complexation starts from the pH ~5.1, which indicates the simultaneous process of complex formation.

The metal hydroxo species also exist in higher pH range ~8.1-9.3 (~10),

$$Ni^{2+} + H_2O \rightleftharpoons Ni(II)(OH)_2 + 2H^+$$

## Ni(II)-Co(II)-Proline-Uracil- ( 1:1:1:1) System

The pH Titration curves and Speciation curves of [Ni(II)-Co(II)-Proline-Uracil] system presented in fig.(4.43) and fig.(4.67) respectively. The inflection of quaternary titration curve (E) from ternary titration curve (D) at pH ~8.2, which shows the complex formation.

Protonated species; $AH_2$, AH, BH; binary, ternary complex species NiAB and CoAB exist in good concentration. The $Ni^{2+}$(aq.) and $Co^{2+}$(aq.), the free metal ions and metal hydroxo species are also present in the system. It is clearly evident from the species distribution curve that the concentration $AH_2$, AH and BH species of both the ligands are decreasing within the pH range ~3.2- 6.5 whereas, BH represented as undissociated species is $[BH]^-$ $\approx$100%. On increasing the pH of the medium, species tend to decrease in its concentration, which shows their involvement in the complex formation.

From distribution profiles, it appear that the binary complexes are formed according to the equilibrium:

$$[AH_2] + Ni^{2+} \rightleftharpoons [Ni(II)\text{-}A] + 2H^+$$

$$[BH]^- + Ni^{2+} \rightleftharpoons [Ni(II)\text{-}BH]^+$$

$$[AH]^- + Co^{2+} \rightleftharpoons [Co(II)\text{-}A] + H^+$$

Speciation curves reveal that binary complex species exist in the system in minimum concentration. With further increase in pH, there is gradual decrease in the concentration of binary complex, this may be due to

the formation of ternary complexes. On the other hand, the binary complex [Zn(II)-Uracil] does not present in the system.

Mixed ligand complexes with $Ni^{2+}$(aq.) is found to be the remarkable species in the pH range ~8.0-10.5, as follows:

$$[AH_2] + Ni^{2+} + [BH]^- \rightleftharpoons [Ni(II)\text{-}A\text{-}BH]^- + 2H^+$$

Further, the formation of ternary complexes with $Ni^{2+}$(aq.) and $Co^{2+}$(aq.) may be stepwise, as it appears. The stepwise formation may be shown as:

$$[Ni(II)\text{-}BH]^+ + [AH]^- \rightleftharpoons [Ni(II)\text{-}A\text{-}BH]^- + H^+$$
$$[Co(II)\text{-}A] + [BH]^- \rightleftharpoons [Co(II)\text{-}A\text{-}BH]^-$$

It may be noticed that the ternary complexes with metal ions complexes show its existence at higher pH. Concentration of ternary NiAB and CoAB increase with concomitant decrease of binary complex species, attaining the maximum concentration $\approx 25\%$ and $\approx 60\%$ respectively.

The multinuclear complex is the predominant species in the present system. The concentration of $Ni^{2+}$ (aq.) and $Co^{2+}$(aq.) metal ions gradually decreases with increase in the pH range ~3.2-9.0, indicating the metal ligand complexation i.e. quaternary complex formation, as follows:

$$[AH]^- + Ni^{2+} + [BH]^- + Co^{2+} \rightleftharpoons [Ni(II)\text{-}Co(II)\text{-}A\text{-}B] + 2H^+$$

The alternative equilibrium is also indicated as:

$$[Ni(II)\text{-}A\text{-}BH]^- + Co^{2+} \rightleftharpoons [Ni(II)\text{-}Co(II)\text{-}A\text{-}B] + H^+$$

$$[Co(II)\text{-}A\text{-}BH]^{-} + Ni^{2+} \rightleftharpoons [Co(II)\text{-}Ni(II)\text{-}A\text{-}B] + H^{+}$$

The concentration of quaternary complex is increasing gradually with the gradual increase in pH and attains a maximum values ≈74% at pH ~8.3. The complexation starts from the pH ~4.6, which shows the simultaneous process of complexation.

Metal hydroxo species viz. $Ni(II)(OH)_2$ and $Co(II)(OH)^{+}$ exist in the system, involving the following equilibrium:

$$Ni^{2+} + 2\,H_2O \rightleftharpoons [Ni(II)(OH)_2] + 2H^{+}$$

$$Co^{2+} + H_2O \rightleftharpoons [Co(II)(OH)]^{+} + H^{+}$$

## Zn(II)-Co-(II)-Proline-Uracil ( 1:1:1:1) System

The Titration curves and Formation curves of [Co(II)-Zn(II)-Proline-Uracil] system presented in fig.(4.44) and fig.(4.68) respectively. In multimetal- multiligand complexation the quaternary complex species, protonated species; $AH_2$, $[AH]^{-}$, $[BH]^{-}$, $Co(OH)^{+}$, $Co(OH)_2$, $Zn(OH)^{+}$, $Zn(OH)_2$, [Co(II)-Proline], [Co(II)-Uracil], [Zn(II)-Proline], [Zn(II)-Uracil], [Co(II)- Proline-Uracil], [Zn(II)-Proline-Uracil], [Co(II)-Zn(II)-Proline-Uracil] and the free metal ions are assumed in the present system. By potentiometric data, it is clearly evident that the complexation of [Co(II)-Zn(II)-A-B] starts at higher pH.

Species distribution curve clearly indicates that the concentration of $AH_2$ and BH species of both the ligands are found to be decreasing with

increase in the pH, whereas, AH is decreasing with the pH range ~4.0-7.0, which shows their involvement in the complex formation.

From speciation curves, it is clear that the binary complexes are formed according to the equilibria:

$$[AH_2] + Zn^{2+} \rightleftharpoons [Zn(II)\text{-}A] + 2H^+$$

$$[BH]^- + Zn^{2+} \rightleftharpoons [Zn(II)\text{-}BH]^+$$

$$[AH]^- + Co^{2+} \rightleftharpoons [Co(II)\text{-}A] + H^+$$

Binary complexes show their existence in the lower pH region and attains the maximum concentration $\approx 25\%, \approx 10\%$ and $\approx 5\%$ respectively. On the other hand, the [Co(II)-Uracil] does not exist in the present system.

The concentration of [Zn(II)-A], [Zn(II)-B] and [Co(II)-A] decreases with further increase in pH, probably due to the formation of ZnAB and CoAB complex species.

Mixed ligand complexes with $Zn^{2+}$(aq.) and $Co^{2+}$(aq.) are found to be the remarkable species in the pH range ~7.7-10.5, as follows:

$$[AH_2] + Zn^{2+} + [BH]^- \rightleftharpoons [Zn(II)\text{-}A\text{-}BH]^- + 2H^+$$

$$[Zn(II)\text{-}BH]^+ + [AH]^- \rightleftharpoons [Zn(II)\text{-}A\text{-}BH]^- + H^+$$

$$[Co(II)\text{-}A] + [BH]^- \rightleftharpoons [Co(II)\text{-}A\text{-}BH]^-$$

For multinuclear system, species distribution curve indicates the formation of heterobinuclear complex according to following equilibrium:

$$[AH_2] + Zn^{2+} + [BH]^- + Co^{2+} \rightleftharpoons [Zn(II)\text{-}Co(II)\text{-}A\text{-}B] + 3H^+$$

The alternative equilibrium is also indicated as follows:

$$[Zn(II)\text{-}A\text{-}BH]^- + Co^{2+} \rightleftharpoons [Zn(II)\text{-}Co(II)\text{-}A\text{-}B] + H^+$$

$$[Co(II)\text{-}A\text{-}BH]^- + Zn^{2+} \rightleftharpoons [Co(II)\text{-}Zn(II)\text{-}A\text{-}B] + H^+$$

It is clear from the speciation curves that there is concomitant decrease in the concentration of $Co^{2+}$ and $Zn^{2+}$ (aqueous ions) with the increase in the concentration of quaternary complex species. The concentration of quaternary complex is increasing gradually with the gradual increase in pH and attains a maximum value $\approx$68% at pH ~7.7.

Metal hydroxo species viz. $Co(II)(OH)_2$ exist in the pH range ~8.1-9.5, involving the following equilibrium:

$$Co^{2+} + 2H_2O \rightleftharpoons [Co(II)(OH)_2] + 2H^+$$

## Cu(II)-Ni(II)-Valine-Thymine -(1:1:1:1) System

Following species have been assumed to exist in the present system fig.(4.45) and fig.(4.69). $[AH_2]$, [AH], $[BH]^-$, $Cu^{2+}$(aq.), $Ni^{2+}$(aq.), hydroxo species $Cu(OH)_2$ and $Ni(OH)_2$, binary complex species i.e. [Cu(II)-A],

$[Ni(II)\text{-}BH]^{+}$, ternary complex species $[Cu(II)\text{-}A\text{-}BH]^{2-}$, $[Ni(II)\text{-}A\text{-}BH]^{2-}$ and multimetal-multiligand complex i.e. [Cu(II)-Ni(II)-A-B] present in the protonated species of both the ligands are present in the decreasing order of concentration showing their involvement with both the metal ions taken understudy, which also follow the declining pattern.

It may be clearly observed that the binary complexes are formed beyond the pH ~8.0. The formation of [Cu(II)-A] starts from pH ~10.4 followed by the gradual increase in its concentration attaining a maximum at pH ~11.0 i.e. 10% . The other binary complex of $Ni^{2+}$ (aq.) shows its existence in the pH range ~8.3-11.0 being approximately ≈25% at pH ~11.0.

Formation equilibria of binary complexes may be assumed to occur as:

$$[AH_2] + Cu^{2+} \rightleftharpoons [Cu(II)\text{-}A] + 2H^{+}$$

$$[AH]^{-} + Cu^{2+} \rightleftharpoons [Cu(II)\text{-}A] + H^{+}$$

$$[BH]^{-} + Ni^{2+} \rightleftharpoons [Ni(II)\text{-}BH]^{+}$$

$$[AH]^{-} + Ni^{2+} \rightleftharpoons [Ni(II)\text{-}A] + H^{+}$$

$$[BH]^{-} + Cu^{2+} \rightleftharpoons [Cu(II)\text{-}B] + H^{+}$$

In the same way, two ternary complexes are formed in appreciable amount in the same pH region. Following two types of ternary complex species are formed:

$$[AH]^{2-} + Cu^{2+} + [BH]^{-} \rightleftharpoons [Cu(II)\text{-}A\text{-}BH]^{2-} + 2H^{+}$$

$$[AH]^{2-} + Ni^{2+} + [BH]^{-} \rightleftharpoons [Ni(II)\text{-}A\text{-}BH]^{2-} + 2H^{+}$$

Maximum concentration of $[Cu(II)\text{-}A\text{-}BH]^{2-}$ species is $\approx 11\%$ at pH ~10.4 while that of $[Ni(II)\text{-}A\text{-}BH]^{2-}$ is $\approx 60\%$ at the same pH.

As is revealed from the species distribution diagram, the quaternary complexation starts at relatively lower pH i.e. <5.0. With the rise in pH, its concentration gradually increases with the decrease in the concentration of protonated ligand species as well as free metal ions. Thus, its formation may be according to the following equation:

$$[AH]^{2-} + Cu^{2+} + [BH]^{-} + Ni^{2+} \rightleftharpoons [Cu(II)\text{-}Ni(II)\text{-}A\text{-}B]^{-} + 2H^{+}$$

Multimetal – multiligand complex shows its maximum abundance $\approx 75\%$ at pH ~9.0 and at still higher pH there is a gradual fall in its concentration. Decline in the concentration of quaternary complex may be explained on the basis of formation of hydroxo species, as metal-ligand formation equilibrium is overlapping with the hydrolytic equilibria of both the metal ions as:

$$Cu^{2+} + 2H_2O \rightleftharpoons Cu(II)(OH)_2 + 2H^{+}$$

$$Ni^{2+} + 2H_2O \rightleftharpoons Ni(II)(OH)_2 + H^+$$

## Cu(II)-Zn(II)-Valine-Thymine (1:1:1:1) System

Fig.(4.46) and fig.(4.70) represent the Titration curves and Speciation curves respectively for [Cu(II)-Zn-(II)-Valine-Thymine] system. Following species are assumed in the present system $AH_2$, AH, BH, $M_1(OH)$, $M_1(OH)_2$, $M_2(OH)$, $M_2(OH)_2$, $M_1A$, $M_1B$, $M_2A$, $M_2B$, $M_1AB$, $M_2AB$ and $M_1M_2AB$.

It is clearly evident form the species distribution curves shows that the concentration of $AH_2$, AH and BH species of both the ligands are found to be in decreasing manner.

Two binary complex species viz.[Cu(II)-Valine] and [Zn(II)-Valine] are formed in the system. The formation of [Cu(II)-Valine] starts at very low pH region but [Zn(II)-Valine] is formed at higher pH range ~7.5-9.0..The complexation equilibrium of binary complexes as follows:

$$[AH]^- + Cu^{2+} \rightleftharpoons [Cu(II)\text{-}A] + H^+$$

$$[AH]^- + Zn^{2+} \rightleftharpoons [Zn(II)\text{-}A] + H^+$$

Mixed ligand complexes $[Cu(II)\text{-}A\text{-}BH]^-$ and $[Zn(II)\text{-}A\text{-}BH]^-$ are found to be major species in the system. Ternary complexes exist in the pH range ~5.5-9.0, while the quaternary complex shows its existence at relatively lower pH region. Ternary complexation occurs as per equilibrium:

$$[AH]^- + Cu^{2+} + [BH]^- \rightleftharpoons [Cu(II)\text{-}A\text{-}BH]^-$$

The another equilibria of ternary complexes as follows:

$$[Cu(II)\text{-}A] + [BH]^- \rightleftharpoons [Cu(II)\text{-}A\text{-}BH]^-$$

$$[Zn(II)\text{-}A] + [BH]^- \rightleftharpoons [Zn(II)\text{-}A\text{-}BH]^-$$

For multinuclear system, the speciation curve indicates the formation of quaternary complex according to the following equilibrium:

$$[AH]^- + Cu^{2+} + [BH]^- + Zn^{2+} \rightleftharpoons [Cu(II)\text{-}Zn(II)\text{-}A\text{-}B]^- + 2H^+$$

The alternative equilibrium is also indicated as follows,

$$[Cu(II)\text{-}A\text{-}BH]^- + Zn^{2+} \rightleftharpoons [Cu(II)\text{-}Zn(II)\text{-}A\text{-}B] + H^+$$

$$[Zn(II)\text{-}A\text{-}BH]^- + Cu^{2+} \rightleftharpoons [Zn(II)\text{-}Cu(II)\text{-}A\text{-}B] + H^+$$

The quaternary [Cu(II)-Zn-(II)-Valine-Thymine] complex is the predominant species in the system. The formation of quaternary species starts at pH ~3.2 and attains the maximum value ≈80% at pH ~7.0. Formation curve clearly indicate that the concentrations of free metal ions viz. $Cu^{2+}$(aq.) and $Zn^{2+}$(aq.) continuously fall in the pH range ~3.3-7.6, which shows their involvement in complexation.

The metal hydroxo are existant in higher pH range ~5.6-9.0 and attaining maximum ≈30%, according to following equilibium:

$$Zn^{2+} + 2H_2O \rightleftharpoons Zn(II)(OH)_2 + 2H^+$$

## Cu(II)-Co-(II)-Valine-Thymine (1:1:1:1) System

Titration curves and Formation curves for [Cu(II)-Co-(II)-Valine-Thymine] system are presented in the fig.(4.47) and fig.(4.71). Multimetal-multiligand complex formation equilibria are found to incorporate quaternary complex species; $AH_2$, AH, BH, binary, ternary complex species, free metal ions and hydroxo species in the present system.

All the protonated ligand species are found to be decreasing with increase in the pH range ~3.3-8.5, which shows their involvement in the complex formation.

[Cu(II)-Valine], [Cu(II)-Thymine] and [Co(II)-Valine] exist in the present system. The formation of metal ligand complexes is indicated by the following equilibria:

$$[AH]^- + Cu^{2+} \rightleftharpoons [Cu(II)\text{-}A] + H^+$$

$$[BH]^- + Cu^{2+} \rightleftharpoons [Cu(II)\text{-}BH]^+$$

$$[AH]^- + Co^{2+} \rightleftharpoons [Co(II)\text{-}A] + H^+$$

The binary complexes [Cu(II)-A] and $[Cu(II)-BH]^+$ are present in the appreciable amount in the pH range ~3.2-9.0. The binary complexation starts in the beginning of titration and the mentioned complexes attain maximum concentration at ≈29% and ≈19% respectively at pH ~4.5. Whereas with further increase in pH, their concentrations decreases.

Mixed ligand complexes with $Cu^{2+}$(aq.) and $Co^{2+}$(aq.) is found to be remarkable species in the higher pH range ~5.4-10.2 as follows:

$$[AH]^- + Cu^{2+} + [BH]^- \rightleftharpoons [Cu(II)\text{-}A\text{-}BH]^- + H^+$$

$$[Cu(II)\text{-}BH]^+ + [AH]^- \rightleftharpoons [Cu(II)\text{-}A\text{-}BH]^- + H^+$$

$$[AH]^- + Co^{2+} + [BH]^- \rightleftharpoons [Co(II)\text{-}A\text{-}BH]^- + H^+$$

For quaternary system, the species distribution curve indicates the formation of heterobinuclear complex according to the following equilibrium:

$$[AH]^- + Cu^{2+} + [BH]^- + Co^{2+} \rightleftharpoons [Cu(II)\text{-}Co(II)\text{-}A\text{-}B] + 2H^+$$

The alternative equilibrium is also indicated as follows,

$$[Cu(II)\text{-}A\text{-}BH]^- + Co^{2+} \rightleftharpoons [Cu(II)\text{-}Co(II)\text{-}A\text{-}B] + H^+$$

$$[Co(II)\text{-}A\text{-}BH]^- + Cu^{2+} \rightleftharpoons [Co(II)\text{-}Cu(II)\text{-}A\text{-}B] + H^+$$

Speciation curve shows that there is a concomitant decline in the concentration of $Cu^{2+}$ and $Co^{2+}$ aqueous ions with the incline in the

concentration of multimetal-multiligand complex species, Quaternary complex species is the predominant species in the present system .The complexation starts from the very beginning and the concentration of multinuclear species is increasing gradually with the gradual increase in pH attaining maximum value ≈77% at pH ~7.5.

Metal hydroxo species $Co(II)(OH)^+$ and $Co(II)(OH)_2$ exist in the pH range ~7.4-10.2 involving the following equilibrium:

$$Co^{2+} + H_2O \rightleftharpoons Co(II)(OH)^+ + H^+$$

$$Co^{2+} + 2H_2O \rightleftharpoons Co(II)(OH)_2 + 2H^+$$

## Ni(II)-Zn(II)-Valine-Thymine -(1:1:1:1) System

Titration curves and Speciation curves for [Ni(II)-Zn(II)-Valine-Thymine] system are presented in fig.(4.48) and fig.(4.72) respectively. Multinuclear species, protonated species; $AH_2$, AH, BH, binary, ternary, free metal ions and hydroxo species exist in considerable amount throughout the entire pH range.

It is clearly evident from the species distribution curves that the protonated ligand $AH_2$, AH and BH species of both the ligands are found to be decreasing with increase in pH in the range ~3.2-7.5. The binary complex species [Ni(II)-Valine], [Zn(II)-Valine] are existing in the higher pH range ~7.8-9.0, while [Ni(II)-Thymine] and [Zn(II)-Thymine] species are absent in the system. The complexation equilibria for binary complexes may be as follows:

$$[AH]^- + Ni^{2+} \rightleftharpoons [Ni(II)\text{-}A] + H^+$$

$$[AH]^- + Zn^{2+} \rightleftharpoons [Zn(II)\text{-}A] + H^+$$

The formation of ternary complex species NiAB and ZnAB ocurrs in the higher pH region ~8.0-9.0. The concentration of mixed ligand complexes incline with increase in pH and attains maximum concentration ≈25% and 10% respectively, according to the following equilibria:

$$[AH]^- + Ni^{2+} + [BH]^- \rightleftharpoons [Ni(II)\text{-}A\text{-}BH]^-$$

$$[AH]^- + Zn^{2+} + [BH]^- \rightleftharpoons [Zn(II)\text{-}A\text{-}BH]^-$$

The alternative step-wise equilibria may be indicated as follows:

$$[Ni(II)\text{-}A] + [BH]^- \rightleftharpoons [Ni(II)\text{-}A\text{-}BH]^-$$

$$[Zn(II)\text{-}A] + [BH]^- \rightleftharpoons [Zn(II)\text{-}A\text{-}BH]^-$$

For multimetal-multiligand system formation curves indicate the complex formation equilibria as follows:

$$[AH]^- + Ni^{2+} + [BH]^- + Zn^{2+} \rightleftharpoons [Ni(II)\text{-}Zn(II)\text{-}A\text{-}B] + 2H^+$$

The another form of equilibria may be represented as:

$$[Ni(II)\text{-}A\text{-}BH]^{-} + Zn^{2+} \rightleftharpoons [Ni(II)\text{-}Zn(II)\text{-}A\text{-}B] + H^{+}$$

Speciation curves clearly reveal that the concentration of free metal ions continuously fall with increase in pH, which shows involvement of free metal ions in the formation of multinuclear complexes. The complexation starts at very low pH region and concentration of quaternary complexes increases with increase in pH and attains maximum value ≈ 85% at pH ~7.6.

The metal hydroxo species also exist in the system between the pH range ~6.9-9.0 and attains maximum value ≈ 50%.

$$Zn^{2+} + 2H_2O \rightleftharpoons Zn(II)(OH)_2 + 2H^{+}$$

## Ni(II)-Co(II)-Valine-Thymine (1:1:1:1) System

Following species have been assumed to exist in the [Ni(II)-Co(II)-Valine-Thymine] which is presented in the fig.(4.73) and fig.(4.49). Protonated species; $AH_2$, AH, BH, $Ni(II)(OH)_2$, $Co(II)(OH)_2$, binary complex species NiA, ternary species NiAB, CoAB and quaternary multinuclear complex species i.e. [Ni(II)-Co(II)-A-B].

The speciation curves clearly show that the concentration of $AH_2$, AH and BH species of both the ligands are present in the decreasing order, showing their involvement with both the metal ions taken under study, which also follow declining pattern.

The binary complex species [Ni(II)-Valine] is formed in very low pH region i.e. the formation of binary complex starts from the very beginning of titration. The concentration of [Ni(II)-Valine] increases with increase in pH and attains maximum value ≈35% at pH ~6.0, whereas [Ni(II)-Thymine] ,

[Co(II)-Valine] and [Co(II)-Thymine], binary complexes are absent in the system. The formation equilibria of binary complex may be assumed to occur as:

$$[AH]^- + Ni^{2+} \rightleftharpoons [Ni(II)\text{-}A] + H^+$$

In the same way two mixed ligand complexes $[Ni(II)\text{-}A\text{-}BH]^-$ and $[Co(II)\text{-}A\text{-}BH]^-$ are formed in appreciable amount at relatively higher pH region. Following two types of ternary complexes are formed:

$$[AH]^- + Ni^{2+} + [BH]^- \rightleftharpoons [Ni(II)\text{-}A\text{-}BH]^- + H^+$$

$$[AH]^- + Co^{2+} + [BH]^- \rightleftharpoons [Co(II)\text{-}A\text{-}BH]^- + H^+$$

The alternative form of equilibrium:

$$[Ni(II)\text{-}A] + [BH]^- \rightleftharpoons [Ni(II)\text{-}A\text{-}BH]^-$$

The complexation equilibria of quaternary complexes assumed to occur as follows:

$$[AH]^- + Ni^{2+} + [BH]^- + Co^{2+} \rightleftharpoons [Ni(II)\text{-}Co(II)\text{-}A\text{-}B] + 2H^+$$

$$[Ni(II)\text{-}A\text{-}BH]^- + Co^{2+} \rightleftharpoons [Ni(II)\text{-}Co(II)\text{-}A\text{-}B] + H^+$$

Formation curve clearly indicates that the quaternary complex species and its maximum abundance ≈76% at pH ~8.0. Decline in concentration of multinuclear complex may be explained on the basis of formation of hydroxo species:

$$Ni^{2+} + 2H_2O \rightleftharpoons Ni(II)(OH)_2 + 2H^+$$

$$Co^{2+} + H_2O \rightleftharpoons Co(II)(OH)^+ + H^+$$

$$Co^{2+} + 2H_2O \rightleftharpoons Co(II)(OH)_2 + 2H^+$$

## Zn(II)-Co(II)-Valine-Thymine (1:1:1:1) System

Titration curves for [Co(II)-Zn(II)-Valine-Thymine] system are presented in fig.(4.50) and Formation curves are represented in fig.(4.74). Multimetal-multiligand complexation equilibrium i.e. quaternary complex species; $AH_2$, AH, BH, binary and ternary exist in good concentration. The free metal ion and hydroxo species are present throughout the entire pH range.

Speciation curve reveals that the concentration of $AH_2$, AH and BH species of both ligands are found to be decreasing with increase in pH in the range ~3.2-8.5, which show their involvement in the complex formation.

The formation of binary complex [Co(II)-Valine] starts at low pH ~3.9 which further increases with increase in pH, whereas, [Zn(II)-Valine], [Zn(II)-Thymine] are formed at higher pH region and attains maximum value ≈15% and 10% respectively at same pH ~8.7.

$$[AH_2] + Zn^{2+} \rightleftharpoons [Zn(II)\text{-}A] + 2H^+$$

$$[AH]^- + Co^{2+} \rightleftharpoons [Co(II)\text{-}A] + H^+$$

$$[BH]^- + Zn^{2+} \rightleftharpoons [Zn(II)\text{-}BH]^+$$

Both [Co(II)-Valine-Thymine] and [Zn(II)-Valine-Thymine] mixed ligand complexes are found to be remarkable species in the pH range ~5.5-10.0 as follows :

$$[AH]^- + Zn^{2+} + [BH]^- \rightleftharpoons [Co(II)\text{-}A\text{-}BH]^- + H^+$$

$$[AH]^- + Co^{2+} + [BH]^- \rightleftharpoons [Zn(II)\text{-}A\text{-}BH]^- + H^+$$

The alternative equilibrium of ternary complexes:

$$[Zn(II)\text{-}A] + [BH]^- \rightleftharpoons [Zn(II)\text{-}A\text{-}BH]^-$$

$$[Co(II)\text{-}A] + [BH]^- \rightleftharpoons [Co(II)\text{-}A\text{-}BH]^-$$

For quaternary system speciation curves indicates the formation of quaternary heterobinuclear complex according to the following equilibrium:

$$[AH]^- + Zn^{2+} + [BH]^- + Co^{2+} \rightleftharpoons [Zn(II)\text{-}Co(II)\text{-}A\text{-}B] + 2H^+$$

The another form of equilibrium is also indicated as follows:

$$[Zn(II)\text{-}A\text{-}BH]^{-} + Zn^{2+} \rightleftharpoons [Zn(II)\text{-}Co(II)\text{-}A\text{-}B] + H^{+}$$

Distribution curves show that there is concomitant decline in the concentration of $Co^{2+}$( aq.) and $Zn^{2+}$(aq.) ions with the incline in the concentration of ternary and quaternary complex species . The concentration of quaternary complex species increases with increase in pH and attaining maximum ≈69% at pH ~7.5.

The metal hydroxo species also formed in the quaternary system which indicates the dissociation of multinuclear complex:

$$Co^{2+} + 2H_2O \rightleftharpoons Co(II)(OH)_2 + 2H^{+}$$

## Cu(II)-Ni(II)-Asparagine-Thymine (1:1:1:1) System

Fig.(4.51) and fig.(4.75) represent the Titration curves and Speciation curves for [Cu(II)-Ni(II)-Asparagine-Thymine] system respectively. The following species are assumed to exist in the quaternary system. Free metal ions, binary, ternary, quaternary complex species and protonated species; $AH_2$, AH and BH of both the ligands the increase in pH from ~3.0-7.4, the concentration of free metal ions $Cu^{2+}$(aq.) and $Ni^{2+}$ (aq.) decreases as the above mentioned protonated ligand species are also following declining pattern of their concentration which shows their involvement in complex formation.

The binary complexes CuB and NiA are present in appreciable amount. The CuB binary complex formation starts from the beginning of titration while NiA starts at higher pH region. The complexation equilibria of binary complexes as follows:

$$[BH]^- + Cu^{2+} \rightleftharpoons [Cu(II)\text{-}BH]^+$$

$$[AH]^- + Ni^{2+} \rightleftharpoons [Ni(II)\text{-}A] + H^+$$

Mixed ligand complexes with $Cu^{2+}$ (aq.) and $Ni^{2+}$(aq.) are found to exist in the range ~7.7-9.3 as follows:

$$[AH]^- + Cu^{2+} + [BH]^- \rightleftharpoons [Cu(II)\text{-}A\text{-}BH]^- + H^+$$

$$[AH]^- + Ni^{2+} + [BH]^- \rightleftharpoons [Ni(II)\text{-}A\text{-}BH]^- + H^+$$

The another form of equilibria can be written as:

$$[Cu(II)\text{-}BH]^+ + [AH]^- \rightleftharpoons [Cu(II)\text{-}A\text{-}BH]^- + H^+$$

$$[Ni(II)\text{-}BH]^- + [AH]^- \rightleftharpoons [Ni(II)\text{-}A\text{-}BH]^- + H^+$$

For multimetal-multiligand system, the species distribution curve indicates the formation of quaternary complex according to the following equilibrium:

$$[AH]^- + Cu^{2+} + [BH]^- + Ni^{2+} \rightleftharpoons [Cu(II)\text{-}Ni(II)\text{-}A\text{-}B] + H^+$$

The alternative equilibrium is also indicated as follows:

$$[Cu(II)\text{-}A\text{-}BH]^{-} + Ni^{2+} \rightleftharpoons [Cu(II)\text{-}Ni(II)\text{-}A\text{-}B] + H^{+}$$

It is evident from the species distribution curve that there is a concomitant decrease in the concentration of $Cu^{2+}$ and $Ni^{2+}$ aqueous ions with the increase in the concentration of quaternary complex being maximum $\approx$95% at pH ~7.0.

The metal hydroxo species viz. $Cu(II)(OH)_2$ and $Ni(II)(OH)_2$ exist in the pH range ~7.0-9.3.

$$Cu^{2+} + 2H_2O \rightleftharpoons Cu(II)(OH)_2 + 2H^{+}$$

$$Ni^{2+} + 2H_2O \rightleftharpoons Ni(II)(OH)_2 + 2H^{+}$$

## Cu(II)-Zn(II)-Asparagine-Thymine ( 1:1:1:1) System

Titration curves and Formation curves for [Cu(II)-Zn(II)-Asparagine-Thymine] system are presented in fig.(4.52) and fig.(4.76) respectively. Multinuclear complex species, protonated ligand species; $AH_2$, AH, BH, binary and ternary complex species viz. $[Cu(II)\text{-}A\text{-}BH]^{-}$ and $[Zn(II)\text{-}A\text{-}BH]^{-}$ exist in good concentration in their usual trend of complexation.

The free metal ions and protonated ligand species of both the ligands have been found to follow a pattern of decreasing concentration with rise in pH. It is clearly evident from Speciation curves that concentration of binary complexes [Cu(II)-Asparagine] and [Cu(II)-Thymine] are maximum in the range ~3.1-4.0, where as concentration of [Zn(II)-Asparagine] is maximum in the pH range ~7.5-9.8, and the species ZnB does not exist at all .

The formation of binary complex may be assumed to follow the equilibrium:

$$[AH_2] + Cu^{2+} \rightleftharpoons [Cu(II)\text{-}A] + 2H^+$$

$$[BH]^- + Cu^{2+} \rightleftharpoons [Cu(II)\text{-}BH]^+$$

$$[AH]^- + Zn^{2+} \rightleftharpoons [Zn(II)\text{-}A] + H^+$$

The concentration of [Cu(II)-Thymine] complex increases gradually attaining the maximum value at pH ~3.8 (≈30%), thereafter there is a gradual decrease in its concentration up to negligible amount at pH ~9.7.

Declining concentration profiles of [Cu(II)-Thymine] and [Cu(II)-Asparagine] indicate the step wise formation of mixed ligand complexes in the pH range ~7.0- 9.3. The complexation equilibria of ternary complexes have been derived on the basis of the speciation curves as follows:

$$[AH]^- + Cu^{2+} + [BH]^- \rightleftharpoons [Cu(II)\text{-}A\text{-}BH]^- + H^+$$

$$[AH]^- + Zn^{2+} + [BH]^- \rightleftharpoons [Zn(II)\text{-}A\text{-}BH]^- + H^+$$

The alternative form of complexation equilibria may be assumed as:

$$[Cu(II)\text{-}A] + [BH]^- \rightleftharpoons [Cu(II)\text{-}A\text{-}BH]^-$$

$$[Zn(II)\text{-}A] + [BH]^- \rightleftharpoons [Zn(II)\text{-}A\text{-}BH]^-$$

Complex formation in a system of two metal ions and two ligands in aqueous solution may be described according to the equilibrium:

$$[AH]^- + Cu^{2+} + [BH]^- + Zn^{2+} \rightleftharpoons [Cu(II)\text{-}Zn(II)\text{-}A\text{-}B] + 2H^+$$

It may be noticed that ternary complexes with metal ions complexes show their existence at higher pH. Concentration of ternary CuAB and ZnAB species increases with concomitant decrease of binary complex species attaining the maximum concentration $\approx$25% and $\approx$60% respectively.

The multinuclear quaternary complex is predominant species in the present system. The concentration of $Cu^{2+}$(aq.) and $Zn^{2+}$(aq.) metal ions gradually decreases with increase in the pH range ~3.2- 9.0 indicating the metal ligand complexation i.e. quaternary complex formation as follows:

$$[AH]^- + Cu^{2+} + [BH]^- + Zn^{2+} \rightleftharpoons [Cu(II)\text{-}Zn(II)\text{-}A\text{-}B] + 2H^+$$

The alternative equilibrium is also indicated as:

$$[Cu(II)\text{-}A\text{-}BH]^- + Zn^{2+} \rightleftharpoons [Cu(II)\text{-}Zn(II)\text{-}A\text{-}B] + H^+$$
$$[Zn(II)\text{-}A\text{-}BH]^- + Cu^{2+} \rightleftharpoons [Zn(II)\text{-}Cu(II)\text{-}A\text{-}B] + H^+$$

It is clearly evident from the speciation curve that there is a gradual decrease in the concentration of $Cu^{2+}$ and $Zn^{2+}$ aqueous ions with the increase in the concentration of quaternary complex species. The

complexation starts from the very beginning of the titration, which shows the simultaneous process of complex formation.

The proportion of hydroxo species are however found to be remarkable at higher pH range. $Cu(II)(OH)_2$ and $Zn(II)(OH)_2$ exist in the system, involving the following equilibrium ,

$$Cu^{2+} + 2H_2O \rightleftharpoons [Cu(II)(OH)_2] + 2H^+$$

$$Zn^{2+} + 2H_2O \rightleftharpoons [Zn(II)(OH)_2] + 2H^+$$

## Cu(II)-Co(II)-Asparagine-Thymine (1:1:1:1) System

Titration curves and Speciation curves for [Cu(II)-Co(II)-Asparagine-Thymine] system are presented in fig.(4.53) and fig.(4.77). The maximum concentration of AH and BH are ≈66% and ≈91% respectively, while the concentration of $AH_2$ ≈90%. The appearance of protonated ligand species in declining manner, which shows their involvement in complex formation. The two major binary complex species i.e. CuA and CuB are existent in the present system. The concentration of species increases with increase in pH and attaining a maximum value ≈32% and ≈9% respectively at same pH, while CoA exist at higher pH. Further increase in pH, the concentration of binary complexes decrease probably due to formation of mixed-ligand complexes. The binary complex formation equilibria may be written as follows:

$$[AH]^- + Co^{2+} \rightleftharpoons [Co(II)\text{-}A] + H^+$$

$$[BH]^- + Cu^{2+} \rightleftharpoons [Cu(II)\text{-}BH]^+$$

$$[AH]^- + Co^{2+} \rightleftharpoons [Co(II)\text{-}A] + H^+$$

Mixed ligand complexes with $Cu^{2+}$ (aq.) and $Co^{2+}$ (aq.) is found to be in the pH range ~7.2-9.5, according to following equilibria:

$$[AH]^- + Cu^{2+} + [BH]^- \rightleftharpoons [Cu(II)\text{-}A\text{-}BH]^- + H^+$$

The alternative equilibrium are also indicated as follows:

$$[Cu(II)\text{-}A] + [BH]^- \rightleftharpoons [Cu(II)\text{-}A\text{-}BH]^-$$

$$[Cu(II)\text{-}BH]^+ + [AH]^- \rightleftharpoons [Cu(II)\text{-}A\text{-}BH]^- + H^+$$

$$[Co(II)\text{-}A] + [BH]^- \rightleftharpoons [Co(II)\text{-}A\text{-}BH]^-$$

For multinuclear system, the Species distribution curve indicates the formation of quaternary complex according to the following equilibrium:

$$[AH]^- + Cu^{2+} + [BH]^- + Co^{2+} \rightleftharpoons [Cu(II)\text{-}Co(II)\text{-}A\text{-}B] + 2H^+$$

The another form of equilibria may be indicated as follows:

$$[Cu(II)\text{-}A\text{-}BH]^{-} + Co^{2+} \rightleftharpoons [Cu(II)\text{-}Co(II)\text{-}A\text{-}B] + H^{+}$$

The speciation curves clearly shows that there is concomitant decline in the concentration of $Cu^{2+}$ and $Co^{2+}$ aqueous ions with the incline in the concentration of quaternary complex species. The maximum value of quaternary species in ≈91% at pH ~7.5. The dissociation of multimetal-multiligand complex due to formation of hydroxo species:

$$Cu^{2+} + 2H_2O \rightleftharpoons Cu(II)(OH)_2 + 2H^{+}$$

$$Co^{2+} + H_2O \rightleftharpoons Co(II)(OH)^{+} + H^{+}$$

$$Co^{2+} + 2H_2O \rightleftharpoons Co(II)(OH)_2 + 2H^{+}$$

## Ni(II)-Zn(II)-Asparagine-Thymine -(1:1:1:1) System

Titration curves and Species distribution curves of the multimetal-multiligand system have been represented in fig.(4.54) and fig. (4.78). The quaternary complex species is the major species in the present system. All the protonated ligand species; $AH_2$, AH and BH found to follow the usual declining pattern with rise in pH. Only [Ni(II)-Asparagine] binary complex exists in the present system. The formation of binary complex starts at higher pH ~7.5 and attains a maximum value ≈20%, whereas formation of [Zn(II)-Thymine] starts at very low pH and increases with increase in pH. The binary complex shows its presence ≈ 20% at pH ~7.0. [Ni(II)-Thymine] and [Zn(II)-Asparagine] do not exist throughout the entire pH range. The

complexation equilibria of binary complex may be explained according to the following equations:

$$[AH]^- + Ni^{2+} \rightleftharpoons [Ni(II)\text{-}A] + H^+$$

$$[BH]^- + Zn^{2+} \rightleftharpoons [Zn(II)\text{-}BH]^+$$

Mixed ligand complex with $Zn^{2+}$ (aq.) is found to be the remarkable species in the pH range ~7.6-8.4 and attains a maximum value ≈25%, whereas [Ni(II)-Asparagine-Thymine] does not exist in the system. From the formation profile it appears that the ternary complex is formed according to the equilibrium:

$$[AH]^- + Zn^{2+} + [BH]^- \rightleftharpoons [Zn(II)\text{-}A\text{-}BH]^-$$

For the present multinuclear system, the speciation curve indicates the formation of heterobinuclear quaternary complex according to the following equilibrium:

$$[AH]^- + Ni^{2+} + [BH]^- + Zn^{2+} \rightleftharpoons [Ni(II)\text{-}Zn(II)\text{-}A\text{-}B] + 2H^+$$

It is clearly evident from distribution curve that declining nature of concentration of $Ni^{2+}$ (aq.) and $Zn^{2+}$ (aq.) shows their involvement or coordination with the ligands. The complexation starts at very low pH ~3.2 and attains maximum value ≈50% at pH ~5.3. The metal hydroxo species formed in the quaternary system follow the following equilibrium:

$$Ni^{2+} + 2H_2O \rightleftharpoons Ni(II)(OH)_2 + 2H^+$$

## Ni(II)-Co(II)-Asparagine-Thymine (1:1:1:1) System

Fig.(4.55) and fig.(4.79) represents the Titration curves and Speciation curves of the multimetal-multiligand system respectively. Following species are assumed in the present system; $AH_2$, AH, BH, $Ni(OH)_2$, $Co(OH)^+$, $Co(OH)_2$, [Ni(II)-Asparagine], [Ni(II)-Thymine], [Ni(II)-Asparagine-Thymine], [Co(II)-Asparagine-Thymine] and [Ni(II)-Co(II)-Asparagine-Thymine]. Among the species assumed, the protonated ligand species; $AH_2$, AH and BH of both the ligands and free metal ions $Ni^{2+}$(aq.) and $Co^{2+}$(aq.) decreases with increase in pH. The coordination of both metal ions with protonated ligand species may be concluded on the basis of increasing concentration of binary, mixed-ligand and multinuclear complex species. It clearly reveals that the concentration of binary complex species i.e. [Ni(II)-Asparagine] and [Ni(II)-Thymine] increases with increase in pH and attains maximum value ≈10% and ≈5% respectively at the same pH. The complexation starts at very low pH, according to following equilibrium:

$$[AH]^- + Ni^{2+} \rightleftharpoons [Ni(II)\text{-}A] + H^+$$

$$[BH]^- + Ni^{2+} \rightleftharpoons [Ni(II)\text{-}BH]^+$$

The formation of mixed ligand complexes start when the concentration of binary complexes decrease. At higher pH ~8.0-10, ternary complexes species viz. [Ni(II)-Aspargine-Thymine] and [Co(II)-Aspargine-Thymine] are existent in the system. From the distribution profile, it appears that the ternary complexes are formed according to the equilibria:

$$[AH]^- + Ni^{2+} + [BH]^- \rightleftharpoons [Ni(II)\text{-}A\text{-}BH]^- + H^+$$

$$[AH]^- + Co^{2+} + [BH]^- \rightleftharpoons [Co(II)\text{-}A\text{-}BH]^- + H^+$$

Formation curve indicates the formation of heterobinuclear quaternary complex according to the following equilibrium:

$$[AH]^- + Ni^{2+} + [BH]^- + Co^{2+} \rightleftharpoons [Ni(II)\text{-}Co(II)\text{-}A\text{-}B] + 2H^+$$

The alternative equilibrium is also indicated as follows:

$$[Ni(II)\text{-}A\text{-}BH]^- + Co^{2+} \rightleftharpoons [Ni(II)\text{-}Co(II)\text{-}A\text{-}B]^- + H^+$$

It is clear from species distribution diagram that quaternary complex species under investigation occur in good concentration along with the binary and ternary species. The multinuclear complex reaches a maximum concentration ≈95% at pH ~8.0. The complex formation starts from the very beginning of titration which shows the simultaneous process complexation. The metal hydroxo species also exist in the system but their concentration is too small. The formation of hydroxo species occurs according to equilibria:

$$Ni^{2+} + 2H_2O \rightleftharpoons Ni(II)(OH)_2 + 2H^+$$

$$Co^{2+} + H_2O \rightleftharpoons Co(II)(OH)^+ + H^+$$

$$Co^{2+} + 2H_2O \rightleftharpoons Co(II)(OH)_2 + 2H^+$$

$$[AH]^- + Ni^{2+} + [BH]^- \rightleftharpoons [Ni(II)\text{-}A\text{-}BH]^- + H^+$$

$$[AH]^- + Co^{2+} + [BH]^- \rightleftharpoons [Co(II)\text{-}A\text{-}BH]^- + H^+$$

Formation curve indicates the formation of heterobinuclear quaternary complex according to the following equilibrium:

$$[AH]^- + Ni^{2+} + [BH]^- + Co^{2+} \rightleftharpoons [Ni(II)\text{-}Co(II)\text{-}A\text{-}B] + 2H^+$$

The alternative equilibrium is also indicated as follows:

$$[Ni(II)\text{-}A\text{-}BH]^- + Co^{2+} \rightleftharpoons [Ni(II)\text{-}Co(II)\text{-}A\text{-}B]^- + H^+$$

It is clear from species distribution diagram that quaternary complex species under investigation occur in good concentration along with the binary and ternary species. The multinuclear complex reaches a maximum concentration ≈95% at pH ~8.0. The complex formation starts from the very beginning of titration which shows the simultaneous process complexation. The metal hydroxo species also exist in the system but their concentration is too small. The formation of hydroxo species occurs according to equilibria:

$$Ni^{2+} + 2H_2O \rightleftharpoons Ni(II)(OH)_2 + 2H^+$$

$$Co^{2+} + H_2O \rightleftharpoons Co(II)(OH)^+ + H^+$$

$$Co^{2+} + 2H_2O \rightleftharpoons Co(II)(OH)_2 + 2H^+$$

## Zn(II)-Co(II)-Asparagine-Thymine (1:1:1:1) System

Speciation curves and Potentiometric curves for [Zn(II)-Co(II)-Asparagine-Thymine] system are presented in fig.(4.56) and fig.(4.80) respectively.

The protonated ligand species, binary, ternary and quaternary complex species are existent in the system. All the protonated species are decreasing with increase in pH. The maximum concentration of the protonated species BH is ≈100% and of AH is ≈93%, whereas, the concentration of $AH_2$ is ≈10%. The concentrations of binary complexes ZnA and CoA are maximum at pH ~7.0, whereas ZnB and CoB do not exist throughout the entire pH range. The complex formation equilibria of binary complexes are as follows:

$$[AH]^- + Zn^{2+} \rightleftharpoons [Zn(II)\text{-}A] + H^+$$

$$[BH]^- + Co^{2+} \rightleftharpoons [Co(II)\text{-}BH]^+$$

The mixed ligand complexes with $Zn^{2+}$(aq.) and $Co^{2+}$(aq.) are found to exist in the pH range ~6.7-9.0 as follows:

$$[AH]^- + Zn^{2+} + [BH]^- \rightleftharpoons [Zn(II)\text{-}A\text{-}BH]^- + H^+$$

$$[AH]^- + Co^{2+} + [BH]^- \rightleftharpoons [Co(II)\text{-}A\text{-}BH]^- + H^+$$

$$[Co(II)\text{-}BH]^+ + [AH]^- \rightleftharpoons [Co(II)\text{-}A\text{-}BH]^- + H^+$$

For quaternary system, the Species distribution curve indicates the formation of heterobinuclear complex according to following equilibria:

$$[AH]^- + Zn^{2+} + [BH]^- + Co^{2+} \rightleftharpoons [Zn(II)\text{-}Co(II)\text{-}A\text{-}B]^- + 2H^+$$

The alternative equilibrium is also indicated as follows:

$$[Zn(II)\text{-}A\text{-}BH]^- + Co^{2+} \rightleftharpoons [Zn(II)\text{-}Co(II)\text{-}A\text{-}B] + H^+$$

$$[Co(II)\text{-}A\text{-}BH]^- + Zn^{2+} \rightleftharpoons [Co(II)\text{-}Zn(II)\text{-}A\text{-}B] + H^+$$

The distribution curves clearly shows that there is a continuous fall in the concentration of $Zn^{2+}$ and $Co^{2+}$ aqueous ions with the rise in concentration of quaternary complex species. The concentration of quaternary complex increases with increase in pH and attains maximum value ≈85% at pH ~7.5.

The appearance of metal hydroxo species indicates the dissociation of quaternary complex. The formation of hydroxo species is as follows:

$$Co^{2+} + 2H_2O \rightleftharpoons Co(II)(OH)_2 + 2H^+$$

**Table 4.17**
**Cu(II) - Ni(II) - Lysine - Uracil - System**

| Volume of NaOH | pH | | | | |
|---|---|---|---|---|---|
| | A | B | C | D | E |
| 0.0 | 2.94 | 2.74 | 2.73 | 2.72 | 3.05 |
| 0.2 | 3.00 | 2.84 | 2.83 | 2.98 | 3.22 |
| 0.4 | 3.27 | 2.97 | 2.97 | 3.17 | 3.60 |
| 0.6 | 4.07 | 3.15 | 3.14 | 3.52 | 4.29 |
| 0.8 | 10.14 | 3.4 | 3.42 | 4.17 | 5.14 |
| 1.0 | 10.54 | 6.77 | 5.80 | 5.03 | 6.37 |
| 1.2 | 10.85 | 8.84 | 6.14 | 6.35 | 7.07 |
| 1.4 | 10.99 | 9.40 | 7.70 | 7.26 | 7.60 |
| 1.6 | 11.03 | 9.87 | 9.51 | 8.16 | 8.15 |
| 1.8 | 11.08 | 10.23 | 10.01 | 8.89 | 8.50 |
| 2.0 | 11.15 | 10.47 | 10.30 | 9.31 | 8.88 |
| 2.2 | 11.20 | 10.64 | 10.51 | 9.65 | 9.30 |
| 2.4 | 11.24 | 10.78 | 10.62 | 9.94 | 9.56 |
| 2.6 | 11.28 | 10.89 | 10.69 | 10.18 | 9.83 |
| 2.8 | | 10.97 | 10.73 | 10.38 | 10.07 |
| 3.0 | | 11.05 | 10.77 | 10.54 | 10.11 |
| 3.2 | | 11.11 | 10.81 | 10.58 | 10.15 |

**Table 4.18**
**Cu(II) - Zn(II) - Lysine - Uracil - System**

| Volume of NaOH | pH | | | | |
|---|---|---|---|---|---|
| | A | B | C | D | E |
| 0.0 | 2.94 | 2.74 | 2.73 | 2.72 | 3.01 |
| 0.2 | 3.00 | 2.84 | 2.83 | 2.98 | 3.21 |
| 0.4 | 3.27 | 2.97 | 2.97 | 3.17 | 3.57 |
| 0.6 | 4.07 | 3.15 | 3.14 | 3.52 | 4.22 |
| 0.8 | 10.14 | 3.4 | 3.42 | 4.17 | 5.04 |
| 1.0 | 10.54 | 6.77 | 5.80 | 5.03 | 6.28 |
| 1.2 | 10.85 | 8.84 | 6.14 | 6.35 | 7.06 |
| 1.4 | 10.99 | 9.40 | 7.70 | 7.26 | 7.40 |
| 1.6 | 11.03 | 9.87 | 9.51 | 8.16 | 7.99 |
| 1.8 | 11.08 | 10.23 | 10.01 | 8.89 | 8.22 |
| 2.0 | 11.15 | 10.47 | 10.30 | 9.31 | 8.66 |
| 2.2 | 11.20 | 10.64 | 10.51 | 9.65 | 9.15 |
| 2.4 | 11.24 | 10.78 | 10.62 | 9.94 | 9.50 |
| 2.6 | 11.28 | 10.89 | 10.69 | 10.18 | 9.84 |
| 2.8 | | 10.97 | 10.73 | 10.38 | 10.15 |
| 3.0 | | 11.05 | 10.77 | 10.54 | 10.22 |
| 3.2 | | 11.11 | 10.81 | 10.58 | 10.27 |
| 3.4 | | 11.15 | 10.85 | 10.62 | 10.31 |

**Table 4.19**
**Cu(II) - Co(II) - Lysine - Uracil - System**

| Volume of NaOH | pH | | | | |
|---|---|---|---|---|---|
| | A | B | C | D | E |
| 0.0 | 2.94 | 2.74 | 2.73 | 2.72 | 3.01 |
| 0.2 | 3.00 | 2.84 | 2.83 | 2.98 | 3.21 |
| 0.4 | 3.27 | 2.97 | 2.97 | 3.17 | 3.57 |
| 0.6 | 4.07 | 3.15 | 3.14 | 3.52 | 4.22 |
| 0.8 | 10.14 | 3.4 | 3.42 | 4.17 | 5.04 |
| 1.0 | 10.54 | 6.77 | 5.80 | 5.03 | 6.28 |
| 1.2 | 10.85 | 8.84 | 6.14 | 6.35 | 7.06 |
| 1.4 | 10.99 | 9.40 | 7.70 | 7.26 | 7.41 |
| 1.6 | 11.03 | 9.87 | 9.51 | 8.16 | 7.89 |
| 1.8 | 11.08 | 10.23 | 10.01 | 8.89 | 8.56 |
| 2.0 | 11.15 | 10.47 | 10.30 | 9.31 | 8.89 |
| 2.2 | 11.20 | 10.64 | 10.51 | 9.65 | 9.34 |
| 2.4 | 11.24 | 10.78 | 10.62 | 9.94 | 9.56 |
| 2.6 | 11.28 | 10.89 | 10.69 | 10.18 | 9.89 |
| 2.8 | | 10.97 | 10.73 | 10.38 | 10.01 |
| 3.0 | | 11.05 | 10.77 | 10.54 | 10.05 |
| 3.2 | | 11.11 | 10.81 | 10.58 | 10.09 |
| 3.4 | | 11.15 | 10.85 | 10.62 | 10.13 |

**Table 4.20**
**Ni(II) - Zn(II) - Lysine - Uracil - System**

| Volume of NaOH | pH | | | | |
|---|---|---|---|---|---|
| | A | B | C | D | E |
| 0.0 | 2.94 | 2.74 | 2.72 | 2.73 | 3.03 |
| 0.2 | 3.00 | 2.84 | 2.82 | 2.99 | 3.25 |
| 0.4 | 3.27 | 2.97 | 2.95 | 3.19 | 3.75 |
| 0.6 | 4.07 | 3.15 | 3.14 | 3.67 | 6.85 |
| 0.8 | 10.14 | 3.4 | 3.51 | 6.41 | 7.47 |
| 1.0 | 10.54 | 6.77 | 6.05 | 7.34 | 7.57 |
| 1.2 | 10.85 | 8.84 | 7.26 | 8.03 | 7.63 |
| 1.4 | 10.99 | 9.40 | 8.09 | 8.65 | 7.97 |
| 1.6 | 11.03 | 9.87 | 9.09 | 8.92 | 8.54 |
| 1.8 | 11.08 | 10.23 | 9.27 | 9.10 | 8.77 |
| 2.0 | 11.15 | 10.47 | 9.59 | 9.39 | 8.99 |
| 2.2 | 11.20 | 10.64 | 9.93 | 9.60 | 9.02 |
| 2.4 | 11.24 | 10.78 | 10.20 | 9.83 | 9.20 |
| 2.6 | 11.28 | 10.89 | 10.41 | 10.05 | 9.36 |
| 2.8 | | 10.97 | 10.56 | 10.25 | 9.56 |
| 3.0 | | 11.05 | 10.69 | 10.41 | 9.84 |
| 3.2 | | 11.11 | 10.80 | 10.45 | 9.89 |
| 3.4 | | 11.15 | 10.85 | 10.50 | 9.95 |

**Table 4.21**
**Ni(II) - Co(II) - Lysine - Uracil - System**

| Volume of NaOH | pH | | | | |
|---|---|---|---|---|---|
| | A | B | C | D | E |
| 0.0 | 2.94 | 2.74 | 2.72 | 2.73 | 3.05 |
| 0.2 | 3.00 | 2.84 | 2.82 | 2.99 | 3.26 |
| 0.4 | 3.27 | 2.97 | 2.95 | 3.19 | 3.73 |
| 0.6 | 4.07 | 3.15 | 3.14 | 3.67 | 6.54 |
| 0.8 | 10.14 | 3.4 | 3.51 | 6.41 | 6.69 |
| 1.0 | 10.54 | 6.77 | 6.05 | 7.34 | 7.89 |
| 1.2 | 10.85 | 8.84 | 7.26 | 8.03 | 7.99 |
| 1.4 | 10.99 | 9.40 | 8.09 | 8.65 | 8.48 |
| 1.6 | 11.03 | 9.87 | 9.09 | 8.92 | 8.52 |
| 1.8 | 11.08 | 10.23 | 9.27 | 9.10 | 8.57 |
| 2.0 | 11.15 | 10.47 | 9.59 | 9.39 | 8.65 |
| 2.2 | 11.20 | 10.64 | 9.93 | 9.60 | 8.75 |
| 2.4 | 11.24 | 10.78 | 10.20 | 9.83 | 9.10 |
| 2.6 | 11.28 | 10.89 | 10.41 | 10.05 | 9.36 |
| 2.8 | | 10.97 | 10.56 | 10.25 | 9.63 |
| 3.0 | | 11.05 | 10.69 | 10.41 | 9.91 |
| 3.2 | | 11.11 | 10.80 | 10.45 | 10.20 |
| 3.4 | | 11.15 | 10.85 | 10.50 | 10.24 |

**Table 4.22**
**Zn(II)- Co(II)- Lysine- Uracil- System**

| Volume of NaOH | pH | | | | |
|---|---|---|---|---|---|
| | A | B | C | D | E |
| 0.0 | 2.94 | 2.74 | 2.73 | 2.98 | 3.03 |
| 0.2 | 3.00 | 2.84 | 2.83 | 3.19 | 3.25 |
| 0.4 | 3.27 | 2.97 | 2.96 | 3.65 | 3.75 |
| 0.6 | 4.07 | 3.15 | 3.14 | 6.88 | 6.85 |
| 0.8 | 10.14 | 3.4 | 3.48 | 7.49 | 7.47 |
| 1.0 | 10.54 | 6.77 | 6.03 | 7.60 | 7.57 |
| 1.2 | 10.85 | 8.84 | 7.51 | 7.69 | 7.63 |
| 1.4 | 10.99 | 9.40 | 7.69 | 7.80 | 7.96 |
| 1.6 | 11.03 | 9.87 | 7.80 | 7.92 | 8.54 |
| 1.8 | 11.08 | 10.23 | 7.88 | 8.09 | 8.77 |
| 2.0 | 11.15 | 10.47 | 8.48 | 8.39 | 8.99 |
| 2.2 | 11.20 | 10.64 | 8.96 | 8.74 | 9.02 |
| 2.4 | 11.24 | 10.78 | 9.41 | 9.04 | 9.20 |
| 2.6 | 11.28 | 10.89 | 9.82 | 9.33 | 9.36 |
| 2.8 | | 10.97 | 10.14 | 9.63 | 9.56 |
| 3.0 | | 11.05 | 10.38 | 9.93 | 9.84 |
| 3.2 | | 11.11 | 10.45 | 10.18 | 9.89 |
| 3.4 | | 11.15 | 10.54 | 10.25 | 9.93 |

**Table – 4.23**

**Cu(II) – Ni(II) –Proline – Uracil - System**

| Volume of NaOH | pH | | | | |
|---|---|---|---|---|---|
| | A | B | C | D | E |
| 0.0 | 2.94 | 2.84 | 2.89 | 3.01 | 3.02 |
| 0.2 | 3.00 | 2.92 | 2.98 | 3.09 | 3.20 |
| 0.4 | 3.27 | 3.03 | 3.09 | 3.25 | 3.57 |
| 0.6 | 4.07 | 3.18 | 3.24 | 3.51 | 4.10 |
| 0.8 | 10.14 | 3.42 | 3.37 | 3.99 | 5.07 |
| 1.0 | 10.54 | 3.97 | 3.82 | 4.81 | 6.11 |
| 1.2 | 10.85 | 9.85 | 7.04 | 5.75 | 7.09 |
| 1.4 | 10.99 | 10.50 | 8.04 | 7.11 | 7.41 |
| 1.6 | 11.03 | 10.81 | 8.96 | 7.62 | 7.81 |
| 1.8 | 11.08 | 10.89 | 9.39 | 8.32 | 8.21 |
| 2.0 | 11.15 | 10.94 | 9.86 | 9.26 | 8.73 |
| 2.2 | 11.20 | 10.99 | 10.16 | 9.88 | 9.07 |
| 2.4 | 11.24 | 11.06 | 10.78 | 10.42 | 9.38 |
| 2.6 | 11.28 | 11.12 | 10.82 | 10.50 | 10.07 |
| 2.8 | | 11.16 | 10.86 | 10.79 | 10.26 |
| 3.0 | | 11.20 | 10.79 | 10.84 | 10.32 |
| 3.2 | | 11.24 | 10.96 | 10.88 | 10.36 |

**Table-4.24**

**Cu(II)-Zn(II) – Proline-Uracil- System**

| Volume of NaOH | pH | | | | |
|---|---|---|---|---|---|
| | A | B | C | D | E |
| 0.0 | 2.94 | 2.84 | 2.89 | 3.01 | 3.03 |
| 0.2 | 3.00 | 2.92 | 2.98 | 3.09 | 3.15 |
| 0.4 | 3.27 | 3.03 | 3.09 | 3.25 | 3.32 |
| 0.6 | 4.07 | 3.18 | 3.24 | 3.51 | 3.61 |
| 0.8 | 10.14 | 3.42 | 3.37 | 3.99 | 4.15 |
| 1.0 | 10.54 | 3.97 | 3.82 | 4.81 | 4.99 |
| 1.2 | 10.85 | 9.85 | 7.04 | 5.75 | 5.97 |
| 1.4 | 10.99 | 10.50 | 8.04 | 7.11 | 7.09 |
| 1.6 | 11.03 | 10.81 | 8.96 | 7.62 | 7.42 |
| 1.8 | 11.08 | 10.89 | 9.39 | 8.32 | 7.72 |
| 2.0 | 11.15 | 10.94 | 9.86 | 9.26 | 8.04 |
| 2.2 | 11.20 | 10.99 | 10.16 | 9.88 | 8.29 |
| 2.4 | 11.24 | 11.06 | 10.78 | 10.42 | 8.84 |
| 2.6 | 11.28 | 11.12 | 10.82 | 10.50 | 9.48 |
| 2.8 | | 11.16 | 10.86 | 10.79 | 10.05 |
| 3.0 | | 11.20 | 10.79 | 10.84 | 10.10 |
| 3.2 | | 11.24 | 10.96 | 10.88 | 10.14 |

**Table-4.25**
**Cu(II)-Co(II)Proline- Uracil -System**

| Volume of NaOH | pH | | | | |
|---|---|---|---|---|---|
| | A | B | C | D | E |
| 0.0 | 2.94 | 2.84 | 2.89 | 3.01 | 3.03 |
| 0.2 | 3.00 | 2.92 | 2.98 | 3.09 | 3.15 |
| 0.4 | 3.27 | 3.03 | 3.09 | 3.25 | 3.32 |
| 0.6 | 4.07 | 3.18 | 3.24 | 3.51 | 3.58 |
| 0.8 | 10.14 | 3.42 | 3.37 | 3.99 | 4.10 |
| 1.0 | 10.54 | 3.97 | 3.82 | 4.81 | 4.93 |
| 1.2 | 10.85 | 9.85 | 7.04 | 5.75 | 5.89 |
| 1.4 | 10.99 | 10.50 | 8.04 | 7.11 | 7.03 |
| 1.6 | 11.03 | 10.81 | 8.96 | 7.62 | 7.34 |
| 1.8 | 11.08 | 10.89 | 9.39 | 8.32 | 7.83 |
| 2.0 | 11.15 | 10.94 | 9.86 | 9.26 | 8.40 |
| 2.2 | 11.20 | 10.99 | 10.16 | 9.88 | 8.78 |
| 2.4 | 11.24 | 11.06 | 10.78 | 10.42 | 8.97 |
| 2.6 | 11.28 | 11.12 | 10.82 | 10.50 | 9.10 |
| 2.8 | | 11.16 | 10.86 | 10.79 | 9.26 |
| 3.0 | | 11.20 | 10.79 | 10.84 | 9.42 |
| 3.2 | | 11.24 | 10.96 | 10.88 | 9.93 |

**Table-4.26**
**Ni(II)-Zn(II) – Proline-Uracil- System**

| Volume of NaOH | pH | | | | |
|---|---|---|---|---|---|
| | A | B | C | D | E |
| 0.0 | 2.94 | 2.84 | 2.87 | 2.99 | 3.03 |
| 0.2 | 3.00 | 2.92 | 2.95 | 3.19 | 3.22 |
| 0.4 | 3.27 | 3.03 | 3.05 | 3.67 | 3.40 |
| 0.6 | 4.07 | 3.18 | 3.19 | 6.41 | 3.70 |
| 0.8 | 10.14 | 3.42 | 3.39 | 7.34 | 5.12 |
| 1.0 | 10.54 | 3.97 | 3.80 | 8.03 | 7.74 |
| 1.2 | 10.85 | 9.85 | 7.02 | 8.65 | 7.97 |
| 1.4 | 10.99 | 10.50 | 8.03 | 8.92 | 8.27 |
| 1.6 | 11.03 | 10.81 | 9.40 | 9.05 | 8.63 |
| 1.8 | 11.08 | 10.89 | 9.80 | 9.39 | 8.86 |
| 2.0 | 11.15 | 10.94 | 9.86 | 9.60 | 9.29 |
| 2.2 | 11.20 | 10.99 | 10.38 | 9.83 | 9.37 |
| 2.4 | 11.24 | 11.06 | 10.76 | 10.05 | 9.48 |
| 2.6 | 11.28 | 11.12 | 10.80 | 10.25 | 9.58 |
| 2.8 | | 11.16 | 10.86 | 10.41 | 9.62 |
| 3.0 | | 11.20 | 10.90 | 10.49 | 9.66 |
| 3.2 | | 11.24 | 10.95 | 10.54 | 9.70 |

**Table-4.27**
**Ni(II)-Co(II) – Proline-Uracil -System**

| Volume of NaOH | pH | | | | |
|---|---|---|---|---|---|
| | A | B | C | D | E |
| 0.0 | 2.94 | 2.84 | 2.87 | 2.99 | 3.04 |
| 0.2 | 3.00 | 2.92 | 2.95 | 3.19 | 3.32 |
| 0.4 | 3.27 | 3.03 | 3.05 | 3.67 | 3.59 |
| 0.6 | 4.07 | 3.18 | 3.19 | 6.41 | 4.68 |
| 0.8 | 10.14 | 3.42 | 3.39 | 7.34 | 7.29 |
| 1.0 | 10.54 | 3.97 | 3.80 | 8.03 | 7.82 |
| 1.2 | 10.85 | 9.85 | 7.02 | 8.65 | 8.27 |
| 1.4 | 10.99 | 10.50 | 8.03 | 8.92 | 8.73 |
| 1.6 | 11.03 | 10.81 | 9.40 | 9.05 | 8.79 |
| 1.8 | 11.08 | 10.89 | 9.80 | 9.39 | 8.88 |
| 2.0 | 11.15 | 10.94 | 9.86 | 9.60 | 8.95 |
| 2.2 | 11.20 | 10.99 | 10.38 | 9.83 | 9.02 |
| 2.4 | 11.24 | 11.06 | 10.76 | 10.05 | 9.07 |
| 2.6 | 11.28 | 11.12 | 10.80 | 10.25 | 9.58 |
| 2.8 | | 11.16 | 10.86 | 10.41 | 9.86 |
| 3.0 | | 11.20 | 10.90 | 10.49 | 10.24 |
| 3.2 | | 11.24 | 10.95 | 10.54 | 10.28 |

**Table-4.28**
**Zn(II)-Co(II)-Proline-Uracil- System**

| Volume of NaOH | pH | | | | |
|---|---|---|---|---|---|
| | A | B | C | D | E |
| 0.0 | 2.94 | 2.84 | 2.89 | 3.01 | 3.05 |
| 0.2 | 3.00 | 2.92 | 2.96 | 3.07 | 3.23 |
| 0.4 | 3.27 | 3.03 | 3.07 | 3.35 | 3.38 |
| 0.6 | 4.07 | 3.18 | 3.21 | 3.63 | 3.67 |
| 0.8 | 10.14 | 3.42 | 3.43 | 4.81 | 4.91 |
| 1.0 | 10.54 | 3.97 | 3.88 | 7.94 | 7.75 |
| 1.2 | 10.85 | 9.85 | 7.43 | 8.08 | 7.94 |
| 1.4 | 10.99 | 10.50 | 7.89 | 8.18 | 7.99 |
| 1.6 | 11.03 | 10.81 | 8.05 | 8.27 | 8.02 |
| 1.8 | 11.08 | 10.89 | 8.73 | 8.35 | 8.26 |
| 2.0 | 11.15 | 10.94 | 8.96 | 8.45 | 8.40 |
| 2.2 | 11.20 | 10.99 | 9.43 | 8.60 | 8.50 |
| 2.4 | 11.24 | 11.06 | 9.83 | 8.89 | 8.66 |
| 2.6 | 11.28 | 11.12 | 10.14 | 9.42 | 8.88 |
| 2.8 | | 11.16 | 10.41 | 9.94 | 9.02 |
| 3.0 | | 11.20 | 10.71 | 10.36 | 9.17 |
| 3.2 | | 11.24 | 10.75 | 10.42 | 9.25 |

**Table-4.27**
**Ni(II)-Co(II) – Proline-Uracil -System**

| Volume of NaOH | pH | | | | |
|---|---|---|---|---|---|
| | A | B | C | D | E |
| 0.0 | 2.94 | 2.84 | 2.87 | 2.99 | 3.04 |
| 0.2 | 3.00 | 2.92 | 2.95 | 3.19 | 3.32 |
| 0.4 | 3.27 | 3.03 | 3.05 | 3.67 | 3.59 |
| 0.6 | 4.07 | 3.18 | 3.19 | 6.41 | 4.68 |
| 0.8 | 10.14 | 3.42 | 3.39 | 7.34 | 7.29 |
| 1.0 | 10.54 | 3.97 | 3.80 | 8.03 | 7.82 |
| 1.2 | 10.85 | 9.85 | 7.02 | 8.65 | 8.27 |
| 1.4 | 10.99 | 10.50 | 8.03 | 8.92 | 8.73 |
| 1.6 | 11.03 | 10.81 | 9.40 | 9.05 | 8.79 |
| 1.8 | 11.08 | 10.89 | 9.80 | 9.39 | 8.88 |
| 2.0 | 11.15 | 10.94 | 9.86 | 9.60 | 8.95 |
| 2.2 | 11.20 | 10.99 | 10.38 | 9.83 | 9.02 |
| 2.4 | 11.24 | 11.06 | 10.76 | 10.05 | 9.07 |
| 2.6 | 11.28 | 11.12 | 10.80 | 10.25 | 9.58 |
| 2.8 | | 11.16 | 10.86 | 10.41 | 9.86 |
| 3.0 | | 11.20 | 10.90 | 10.49 | 10.24 |
| 3.2 | | 11.24 | 10.95 | 10.54 | 10.28 |

**Table-4.28**
**Zn(II)-Co(II)-Proline-Uracil- System**

| Volume of NaOH | pH | | | | |
|---|---|---|---|---|---|
| | A | B | C | D | E |
| 0.0 | 2.94 | 2.84 | 2.89 | 3.01 | 3.05 |
| 0.2 | 3.00 | 2.92 | 2.96 | 3.07 | 3.23 |
| 0.4 | 3.27 | 3.03 | 3.07 | 3.35 | 3.38 |
| 0.6 | 4.07 | 3.18 | 3.21 | 3.63 | 3.67 |
| 0.8 | 10.14 | 3.42 | 3.43 | 4.81 | 4.91 |
| 1.0 | 10.54 | 3.97 | 3.88 | 7.94 | 7.75 |
| 1.2 | 10.85 | 9.85 | 7.43 | 8.08 | 7.94 |
| 1.4 | 10.99 | 10.50 | 7.89 | 8.18 | 7.99 |
| 1.6 | 11.03 | 10.81 | 8.05 | 8.27 | 8.02 |
| 1.8 | 11.08 | 10.89 | 8.73 | 8.35 | 8.26 |
| 2.0 | 11.15 | 10.94 | 8.96 | 8.45 | 8.40 |
| 2.2 | 11.20 | 10.99 | 9.43 | 8.60 | 8.50 |
| 2.4 | 11.24 | 11.06 | 9.83 | 8.89 | 8.66 |
| 2.6 | 11.28 | 11.12 | 10.14 | 9.42 | 8.88 |
| 2.8 | | 11.16 | 10.41 | 9.94 | 9.02 |
| 3.0 | | 11.20 | 10.71 | 10.36 | 9.17 |
| 3.2 | | 11.24 | 10.75 | 10.42 | 9.25 |

**Table-4.29**
**Cu(II)- Ni(II)-Valine-Thymine-System**

| Volume of NaOH | pH | | | | |
|---|---|---|---|---|---|
| | A | B | C | D | E |
| 0.0 | 2.94 | 2.82 | 3.00 | 3.03 | 3.02 |
| 0.2 | 3.00 | 2.94 | 3.25 | 3.13 | 3.35 |
| 0.4 | 3.27 | 3.12 | 3.67 | 3.32 | 3.65 |
| 0.6 | 4.07 | 3.39 | 4.26 | 3.61 | 4.13 |
| 0.8 | 10.14 | 8.95 | 6.48 | 5.47 | 4.76 |
| 1.0 | 10.54 | 9.56 | 6.84 | 6.61 | 5.55 |
| 1.2 | 10.85 | 10.03 | 8.56 | 7.78 | 6.70 |
| 1.4 | 10.99 | 10.36 | 8.98 | 8.78 | 7.37 |
| 1.6 | 11.03 | 10.57 | 10.00 | 8.94 | 8.04 |
| 1.8 | 11.08 | 10.70 | 10.30 | 9.61 | 8.34 |
| 2.0 | 11.15 | 10.82 | 10.50 | 10.03 | 8.97 |
| 2.2 | 11.20 | 10.90 | 10.75 | 10.35 | 9.57 |
| 2.4 | 11.24 | 11.02 | 10.86 | 10.57 | 9.98 |
| 2.6 | 11.28 | 11.08 | 10.90 | 10.74 | 10.28 |
| 2.8 | 11.32 | 11.12 | 10.98 | 10.78 | 10.51 |
| 3.0 | 11.36 | 11.16 | 11.02 | 10.82 | 10.56 |
| 3.2 | 11.40 | 11.20 | 10.06 | 10.86 | 10.60 |

**Table-4.30**
**Cu(II)-Zn(II)-Valine-Thymine-System**

| Volume of NaOH | pH | | | | |
|---|---|---|---|---|---|
| | A | B | C | D | E |
| 0.0 | 2.94 | 2.82 | 3.00 | 3.03 | 3.04 |
| 0.2 | 3.00 | 2.94 | 3.25 | 3.13 | 3.34 |
| 0.4 | 3.27 | 3.12 | 3.67 | 3.32 | 3.62 |
| 0.6 | 4.07 | 3.39 | 4.26 | 3.61 | 4.09 |
| 0.8 | 10.14 | 8.95 | 6.48 | 5.47 | 4.72 |
| 1.0 | 10.54 | 9.56 | 6.84 | 6.61 | 5.12 |
| 1.2 | 10.85 | 10.03 | 8.56 | 7.78 | 6.74 |
| 1.4 | 10.99 | 10.36 | 8.98 | 8.78 | 7.48 |
| 1.6 | 11.03 | 10.57 | 10.00 | 8.94 | 8.09 |
| 1.8 | 11.08 | 10.70 | 10.30 | 9.61 | 8.39 |
| 2.0 | 11.15 | 10.82 | 10.50 | 10.03 | 8.19 |
| 2.2 | 11.20 | 10.90 | 10.75 | 10.35 | 9.69 |
| 2.4 | 11.24 | 11.02 | 10.86 | 10.57 | 10.03 |
| 2.6 | 11.28 | 11.08 | 10.90 | 10.74 | 10.34 |
| 2.8 | | 11.12 | 10.98 | 10.78 | 10.55 |
| 3.0 | | 11.16 | 11.02 | 10.82 | 10.61 |
| 3.2 | | 11.20 | 11.06 | 10.86 | 10.65 |

**Table-4.31**
**Cu(II) –Co(II) –Valine-Thymine-System**

| Volume of NaOH | pH | | | | |
|---|---|---|---|---|---|
| | A | B | C | D | E |
| 0.0 | 2.94 | 2.82 | 3.00 | 3.03 | 3.05 |
| 0.2 | 3.00 | 2.94 | 3.25 | 3.13 | 3.36 |
| 0.4 | 3.27 | 3.12 | 3.67 | 3.32 | 3.65 |
| 0.6 | 4.07 | 3.39 | 4.26 | 3.61 | 4.08 |
| 0.8 | 10.14 | 8.95 | 6.48 | 5.47 | 4.67 |
| 1.0 | 10.54 | 9.56 | 6.84 | 6.61 | 5.39 |
| 1.2 | 10.85 | 10.03 | 8.56 | 7.78 | 6.43 |
| 1.4 | 10.99 | 10.36 | 8.98 | 8.78 | 7.45 |
| 1.6 | 11.03 | 10.57 | 10.00 | 8.94 | 8.96 |
| 1.8 | 11.08 | 10.70 | 10.30 | 9.61 | 9.20 |
| 2.0 | 11.15 | 10.82 | 10.50 | 10.03 | 9.56 |
| 2.2 | 11.20 | 10.90 | 10.75 | 10.35 | 9.94 |
| 2.4 | 11.24 | 11.02 | 10.86 | 10.57 | 10.25 |
| 2.6 | 11.28 | 11.08 | 10.90 | 10.74 | 10.48 |
| 2.8 | | 11.12 | 10.98 | 10.78 | 10.52 |
| 3.0 | | 11.16 | 11.02 | 10.82 | 10.57 |
| 3.2 | | 11.20 | 11.06 | 10.86 | 10.62 |

**Table-4.32**
**ZnII) – Co(II) –Valine-Thymine-System**

| Volume of NaOH | pH | | | | |
|---|---|---|---|---|---|
| | A | B | C | D | E |
| 0.0 | 2.94 | 2.82 | 2.73 | 3.06 | 3.07 |
| 0.2 | 3.00 | 2.94 | 2.82 | 3.20 | 3.20 |
| 0.4 | 3.27 | 3.12 | 2.94 | 3.44 | 3.41 |
| 0.6 | 4.07 | 3.39 | 3.12 | 3.98 | 3.83 |
| 0.8 | 10.14 | 8.95 | 3.39 | 6.92 | 6.54 |
| 1.0 | 10.54 | 9.56 | 4.40 | 7.51 | 7.38 |
| 1.2 | 10.85 | 10.03 | 7.95 | 7.64 | 7.56 |
| 1.4 | 10.99 | 10.36 | 8.96 | 7.77 | 7.62 |
| 1.6 | 11.03 | 10.57 | 10.09 | 8.51 | 7.93 |
| 1.8 | 11.08 | 10.70 | 10.46 | 8.94 | 8.04 |
| 2.0 | 11.15 | 10.82 | 10.67 | 9.56 | 8.16 |
| 2.2 | 11.20 | 10.90 | 10.73 | 9.80 | 8.32 |
| 2.4 | 11.24 | 11.02 | 10.80 | 10.04 | 8.75 |
| 2.6 | 11.28 | 11.08 | 10.90 | 10.25 | 9.45 |
| 2.8 | 11.32 | 11.12 | 10.96 | 10.50 | 9.56 |
| 3.0 | 11.36 | 11.16 | 11.01 | 10.56 | 9.60 |
| 3.2 | 11.40 | 11.20 | | 10.60 | 9.64 |

**Table-4.33**
**Ni(II) –ZnII) –Valine-Thymine-System**

| Volume of NaOH | pH | | | | |
|---|---|---|---|---|---|
| | A | B | C | D | E |
| 0.0 | 2.94 | 2.82 | 2.72 | 2.99 | 3.06 |
| 0.2 | 3.00 | 2.94 | 2.82 | 3.15 | 3.19 |
| 0.4 | 3.27 | 3.12 | 2.94 | 3.39 | 3.41 |
| 0.6 | 4.07 | 3.39 | 3.12 | 6.41 | 3.93 |
| 0.8 | 10.14 | 8.95 | 3.39 | 7.12 | 6.89 |
| 1.0 | 10.54 | 9.56 | 4.40 | 7.21 | 7.10 |
| 1.2 | 10.85 | 10.03 | 8.95 | 7.95 | 7.64 |
| 1.4 | 10.99 | 10.36 | 9.56 | 8.65 | 7.93 |
| 1.6 | 11.03 | 10.57 | 10.03 | 9.20 | 8.05 |
| 1.8 | 11.08 | 10.70 | 10.36 | 9.37 | 8.43 |
| 2.0 | 11.15 | 10.82 | 10.57 | 9.62 | 8.65 |
| 2.2 | 11.20 | 10.90 | 10.70 | 9.86 | 9.45 |
| 2.4 | 11.24 | 11.02 | 10.82 | 10.07 | 9.75 |
| 2.6 | 11.28 | 11.08 | 10.90 | 10.30 | 9.83 |
| 2.8 | | 11.12 | 11.02 | 10.46 | 9.90 |
| 3.0 | | 11.16 | 11.08 | 10.74 | 9.94 |
| 3.2 | | 11.20 | 11.12 | 10.78 | 9.98 |

**Table-4.34**
**Ni(II) –Co(II) –Valine-Thymine-System**

| Volume of NaOH | pH | | | | |
|---|---|---|---|---|---|
| | A | B | C | D | E |
| 0.0 | 2.94 | 2.82 | 2.72 | 2.99 | 3.03 |
| 0.2 | 3.00 | 2.94 | 2.82 | 3.15 | 3.17 |
| 0.4 | 3.27 | 3.12 | 2.94 | 3.39 | 3.38 |
| 0.6 | 4.07 | 3.39 | 3.12 | 6.41 | 3.77 |
| 0.8 | 10.14 | 8.95 | 3.39 | 7.12 | 6.05 |
| 1.0 | 10.54 | 9.56 | 4.40 | 7.21 | 7.04 |
| 1.2 | 10.85 | 10.03 | 8.95 | 7.95 | 7.63 |
| 1.4 | 10.99 | 10.36 | 9.56 | 8.65 | 8.22 |
| 1.6 | 11.03 | 10.57 | 10.03 | 9.20 | 8.54 |
| 1.8 | 11.08 | 10.70 | 10.36 | 9.37 | 8.60 |
| 2.0 | 11.15 | 10.82 | 10.57 | 9.62 | 8.67 |
| 2.2 | 11.20 | 10.90 | 10.70 | 9.86 | 9.96 |
| 2.4 | 11.24 | 11.02 | 10.82 | 10.07 | 9.20 |
| 2.6 | 11.28 | 11.08 | 10.90 | 10.30 | 9.47 |
| 2.8 | | 11.12 | 11.02 | 10.46 | 10.17 |
| 3.0 | | 11.16 | 11.08 | 10.74 | 10.28 |
| 3.2 | | 11.20 | 11.12 | 10.78 | 10.32 |

**Table-4.35**
**Cu(II) – Ni(II) –Asparagine-Thymine -System**

| Volume of NaOH | pH | | | | |
|---|---|---|---|---|---|
| | A | B | C | D | E |
| 0.0 | 2.94 | 2.80 | 2.79 | 2.96 | 3.03 |
| 0.2 | 3.00 | 2.90 | 2.85 | 3.14 | 3.18 |
| 0.4 | 3.27 | 3.19 | 2.91 | 3.41 | 3.42 |
| 0.6 | 4.07 | 8.42 | 3.09 | 3.86 | 4.52 |
| 0.8 | 10.14 | 9.40 | 3.35 | 4.62 | 6.00 |
| 1.0 | 10.54 | 9.91 | 4.46 | 6.63 | 6.94 |
| 1.2 | 10.85 | 10.26 | 8.22 | 7.43 | 7.37 |
| 1.4 | 10.99 | 10.52 | 8.87 | 8.56 | 7.79 |
| 1.6 | 11.03 | 10.65 | 9.61 | 9.35 | 8.26 |
| 1.8 | 11.08 | 10.81 | 10.24 | 9.77 | 8.69 |
| 2.0 | 11.15 | 10.90 | 10.55 | 10.09 | 9.13 |
| 2.2 | 11.20 | 10.98 | 10.73 | 10.34 | 9.50 |
| 2.4 | 11.24 | 11.10 | 10.86 | 10.52 | 9.80 |
| 2.6 | 11.28 | 11.15 | 10.96 | 10.68 | 10.06 |
| 2.8 | | 11.20 | 11.04 | 10.80 | 10.29 |
| 3.0 | | 11.16 | 11.10 | 10.90 | 10.45 |
| 3.2 | | 11.24 | 10.15 | 10.97 | 10.58 |

**Table-4.36**
**Cu(II) – Zn(II) –Asparagine-Thymine- System**

| Volume of NaOH | pH | | | | |
|---|---|---|---|---|---|
| | A | B | C | D | E |
| 0.0 | 2.94 | 2.80 | 2.79 | 2.96 | 3.04 |
| 0.2 | 3.00 | 2.90 | 2.85 | 3.14 | 3.21 |
| 0.4 | 3.27 | 3.19 | 2.91 | 3.41 | 3.47 |
| 0.6 | 4.07 | 8.42 | 3.09 | 3.86 | 3.90 |
| 0.8 | 10.14 | 9.40 | 3.35 | 4.62 | 4.66 |
| 1.0 | 10.54 | 9.91 | 4.46 | 6.63 | 6.42 |
| 1.2 | 10.85 | 10.26 | 8.22 | 7.43 | 7.03 |
| 1.4 | 10.99 | 10.52 | 8.87 | 8.56 | 7.29 |
| 1.6 | 11.03 | 10.65 | 9.61 | 9.35 | 7.40 |
| 1.8 | 11.08 | 10.81 | 10.24 | 9.77 | 7.47 |
| 2.0 | 11.15 | 10.90 | 10.55 | 10.09 | 7.57 |
| 2.2 | 11.20 | 10.98 | 10.73 | 10.34 | 7.67 |
| 2.4 | 11.24 | 11.10 | 10.86 | 10.52 | 7.88 |
| 2.6 | 11.28 | 11.15 | 10.96 | 10.68 | 8.28 |
| 2.8 | | 11.20 | 11.04 | 10.80 | 9.00 |
| 3.0 | | 11.16 | 11.10 | 10.90 | 9.48 |
| 3.2 | | 11.24 | 10.15 | 10.97 | 9.56 |

## Table-4.37
## Cu(II) – Co(II) –Asparagine-Thymine- System

| Volume of NaOH | pH | | | | |
|---|---|---|---|---|---|
| | A | B | C | D | E |
| 0.0 | 2.94 | 2.80 | 2.79 | 2.96 | 3.04 |
| 0.2 | 3.00 | 2.90 | 2.85 | 3.14 | 3.21 |
| 0.4 | 3.27 | 3.19 | 2.91 | 3.41 | 3.46 |
| 0.6 | 4.07 | 8.42 | 3.09 | 3.86 | 3.88 |
| 0.8 | 10.14 | 9.40 | 3.35 | 4.62 | 4.63 |
| 1.0 | 10.54 | 9.91 | 4.46 | 6.63 | 6.41 |
| 1.2 | 10.85 | 10.26 | 8.22 | 7.43 | 7.12 |
| 1.4 | 10.99 | 10.52 | 8.87 | 8.56 | 7.66 |
| 1.6 | 11.03 | 10.65 | 9.61 | 9.35 | 8.00 |
| 1.8 | 11.08 | 10.81 | 10.24 | 9.77 | 8.50 |
| 2.0 | 11.15 | 10.90 | 10.55 | 10.09 | 8.76 |
| 2.2 | 11.20 | 10.98 | 10.73 | 10.34 | 8.97 |
| 2.4 | 11.24 | 11.10 | 10.86 | 10.52 | 9.27 |
| 2.6 | 11.28 | 11.15 | 10.96 | 10.68 | 9.60 |
| 2.8 | | 11.20 | 11.04 | 10.80 | 9.90 |
| 3.0 | | 11.16 | 11.10 | 10.90 | 10.15 |
| 3.2 | | 11.24 | 10.15 | 10.97 | 10.35 |

## Table-4.38
## Ni(II) – Zn(II) –Asparagine-Thymine- System

| Volume of NaOH | pH | | | | |
|---|---|---|---|---|---|
| | A | B | C | D | E |
| 0.0 | 2.94 | 2.80 | 2.75 | 2.99 | 3.07 |
| 0.2 | 3.00 | 2.90 | 2.83 | 3.20 | 3.31 |
| 0.4 | 3.27 | 3.19 | 2.96 | 3.68 | 3.83 |
| 0.6 | 4.07 | 8.42 | 3.15 | 5.54 | 5.51 |
| 0.8 | 10.14 | 9.40 | 5.12 | 6.44 | 6.32 |
| 1.0 | 10.54 | 9.91 | 6.22 | 7.50 | 7.3 |
| 1.2 | 10.85 | 10.26 | 7.13 | 8.92 | 7.44 |
| 1.4 | 10.99 | 10.52 | 9.04 | 9.26 | 7.52 |
| 1.6 | 11.03 | 10.65 | 9.86 | 9.53 | 7.55 |
| 1.8 | 11.08 | 10.81 | 10.20 | 9.79 | 7.67 |
| 2.0 | 11.15 | 10.90 | 10.48 | 10.09 | 7.74 |
| 2.2 | 11.20 | 10.98 | 10.63 | 10.29 | 7.95 |
| 2.4 | 11.24 | 11.10 | 10.74 | 10.50 | 8.28 |
| 2.6 | 11.28 | 11.15 | 10.80 | 10.64 | 8.6 |
| 2.8 | | 11.20 | 10.85 | 10.75 | 9.05 |
| 3.0 | | 11.16 | 10.90 | 10.83 | 9.76 |
| 3.2 | | 11.24 | 10.94 | 10.92 | 9.89 |

**Table 4.39**
**Ni(II)- Co(II)- Asparagine-Thymine -system**

| Volume of NaOH | pH | | | | |
|---|---|---|---|---|---|
| | A | B | C | D | E |
| 0.0 | 2.94 | 2.80 | 2.75 | 2.99 | 3.08 |
| 0.2 | 3.00 | 2.90 | 2.83 | 3.2 | 3.29 |
| 0.4 | 3.27 | 3.19 | 2.96 | 3.68 | 3.81 |
| 0.6 | 4.07 | 8.42 | 3.15 | 5.54 | 5.45 |
| 0.8 | 10.14 | 9.40 | 5.12 | 6.44 | 6.28 |
| 1.0 | 10.54 | 9.91 | 6.22 | 7.5 | 7.31 |
| 1.2 | 10.85 | 10.26 | 7.13 | 8.92 | 8.3 |
| 1.4 | 10.99 | 10.52 | 9.04 | 9.26 | 8.33 |
| 1.6 | 11.03 | 10.65 | 9.86 | 9.53 | 8.44 |
| 1.8 | 11.08 | 10.81 | 10.2 | 9.79 | 8.56 |
| 2.0 | 11.15 | 10.90 | 10.48 | 10.09 | 8.72 |
| 2.2 | 11.20 | 10.98 | 10.63 | 10.29 | 8.98 |
| 2.4 | 11.24 | 11.10 | 10.74 | 10.5 | 9.33 |
| 2.6 | 11.28 | 11.15 | 10.8 | 10.64 | 9.66 |
| 2.8 | | 11.20 | 10.85 | 10.75 | 9.96 |
| 3.0 | | 11.16 | 10.9 | 10.83 | 10.18 |
| 3.2 | | 11.24 | 10.94 | 10.92 | 10.37 |

**Table 4.40**
**Zn(II)- Co(II)- Asparagine-Thymine- system**

| Volume of NaOH | pH | | | | |
|---|---|---|---|---|---|
| | A | B | C | D | E |
| 0.0 | 2.94 | 2.80 | 2.74 | 3.01 | 3.08 |
| 0.2 | 3.00 | 2.90 | 2.84 | 3.24 | 3.32 |
| 0.4 | 3.27 | 3.19 | 2.98 | 3.81 | 3.94 |
| 0.6 | 4.07 | 8.42 | 3.57 | 3.99 | 6.1 |
| 0.8 | 10.14 | 9.40 | 5.58 | 6.3 | 6.82 |
| 1.0 | 10.54 | 9.91 | 7.75 | 7.09 | 7.39 |
| 1.2 | 10.85 | 10.26 | 7.9 | 7.64 | 7.45 |
| 1.4 | 10.99 | 10.52 | 8.03 | 7.8 | 7.53 |
| 1.6 | 11.03 | 10.65 | 8.24 | 7.96 | 7.58 |
| 1.8 | 11.08 | 10.81 | 8.54 | 8.12 | 7.69 |
| 2.0 | 11.15 | 10.90 | 8.91 | 8.35 | 7.8 |
| 2.2 | 11.20 | 10.98 | 9.3 | 8.65 | 7.97 |
| 2.4 | 11.24 | 11.10 | 9.71 | 8.97 | 8.18 |
| 2.6 | 11.28 | 11.15 | 9.78 | 9.23 | 8.45 |
| 2.8 | | 11.20 | 9.86 | 9.53 | 8.65 |
| 3.0 | | 11.16 | 10.09 | 9.85 | 8.96 |
| 3.2 | | 11.24 | 10.14 | 9.89 | 9.25 |

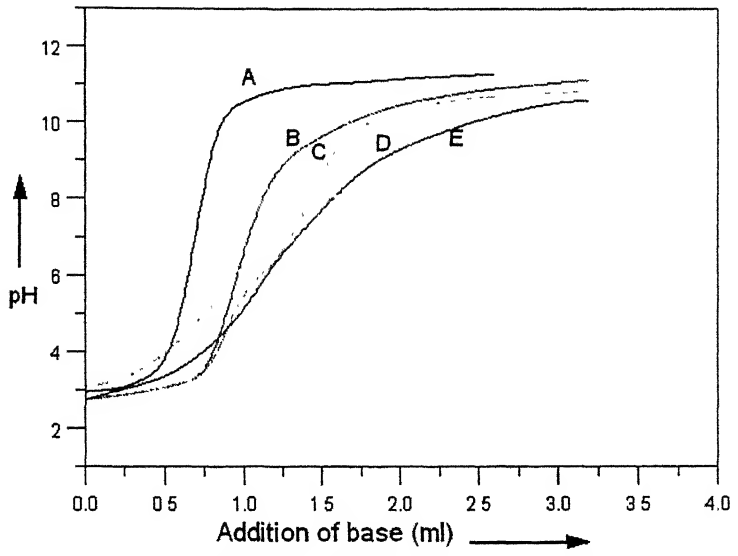



Fig.4.33- Potentiometric titration Curves of 1:1:1:1 Cu(II)-Ni(II)-Lysine-Uracil system; (A) Acid (B) Lysine (C) Cu(II)-Lysine (D) Cu(II)-Lysine-Uracil (E) Cu(II)-Ni(II)- Lysine- Uracil

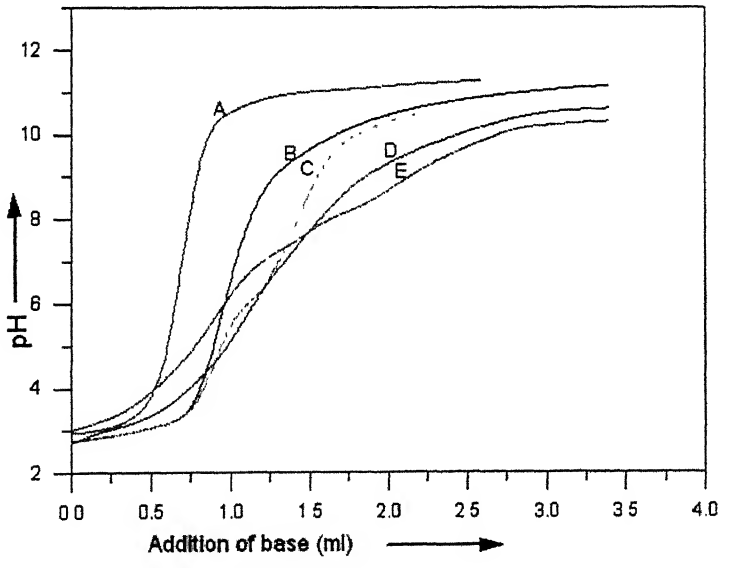



Fig.4.34- Potentiometric titration Curves of 1:1:1:1 Cu(II)-Zn(II)-Lysine-Uracil system; (A) Acid (B) Lysine (C) Cu(II)-Lysine (D) Cu(II)-Lysine-Uracil (E) Cu(II)-Zn(II)- Lysine- Uracil

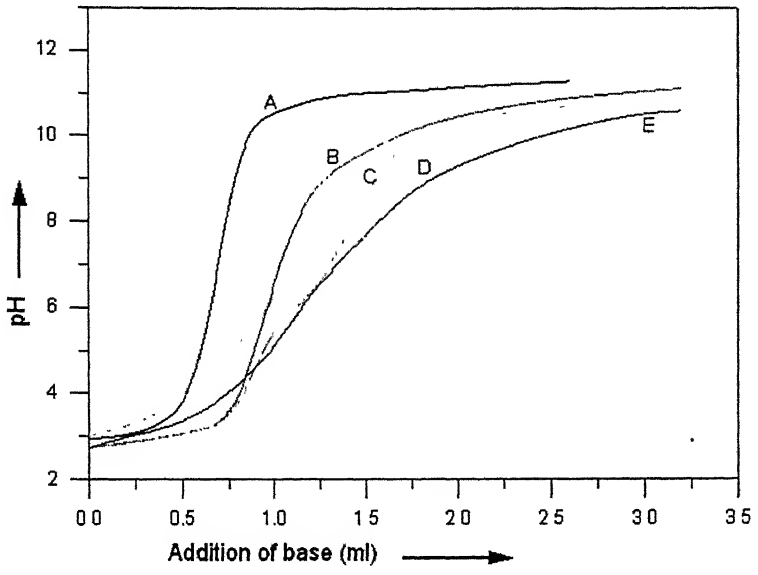



Fig.4.35- Potentiometric titration Curves of 1:1:1:1 Cu(II)-Co(II)-Lysine-Uracil system; (A) Acid (B) Lysine (C) Cu(II)-Lysine (D) Cu(II)-Lysine-Uracil (E) Cu(II)-Co(II)- Lysine- Uracil

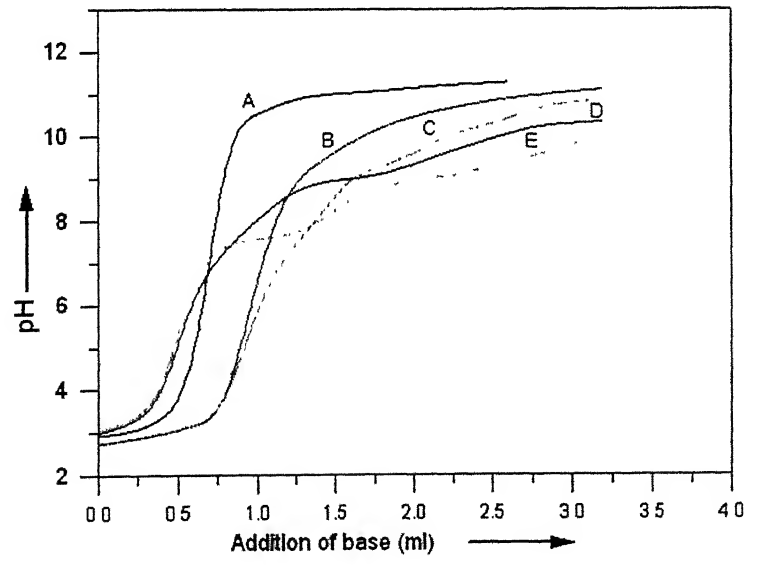



Fig.4.36- Potentiometric titration Curves of 1:1:1:1 Ni(II)-Zn(II)-Lysine-Uracil system; (A) Acid (B) Lysine (C) Ni(II)-Lysine (D) Ni(II)-Lysine-Uracil (E) Ni(II)-Zn(II)- Lysine- Uracil

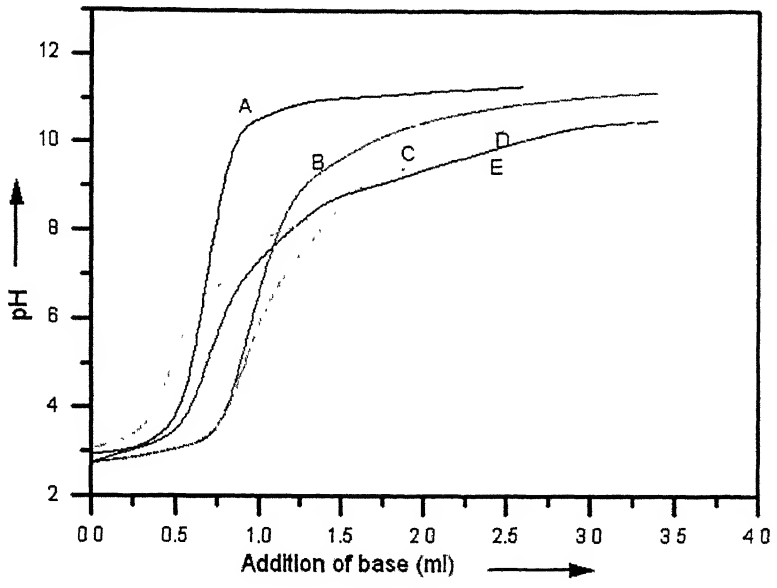



Fig.4.37- Potentiometric titration Curves of 1:1:1:1 Ni(II)-Co(II)-Lysine-Uracil system; (A) Acid (B) Lysine (C) Ni(II)-Lysine (D) Ni(II)-Lysine-Uracil (E) Ni(II)-Co(II)- Lysine- Uracil

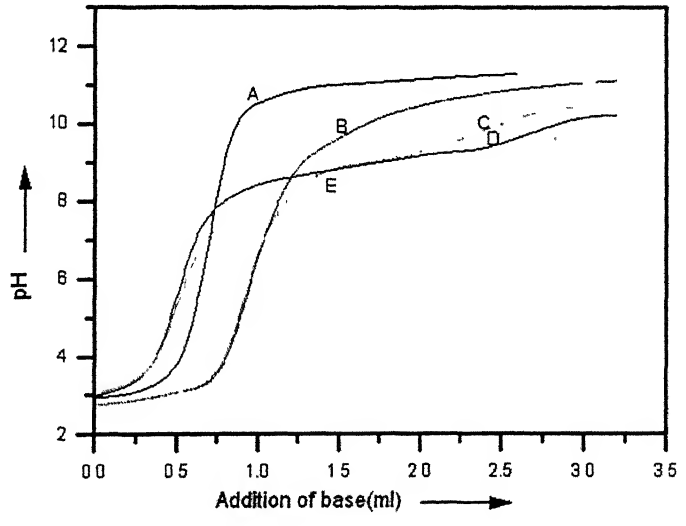



Fig.4.38- Potentiometric titration Curves of 1:1:1:1 Zn(II)-Co(II)- Lysine-Uracil system; (A) Acid (B) Lysine (C) Zn(II)-Lysine (D) Zn(II)-Lysine-Uracil (E) Zn(II)-Co(II)- Lysine- Uracil

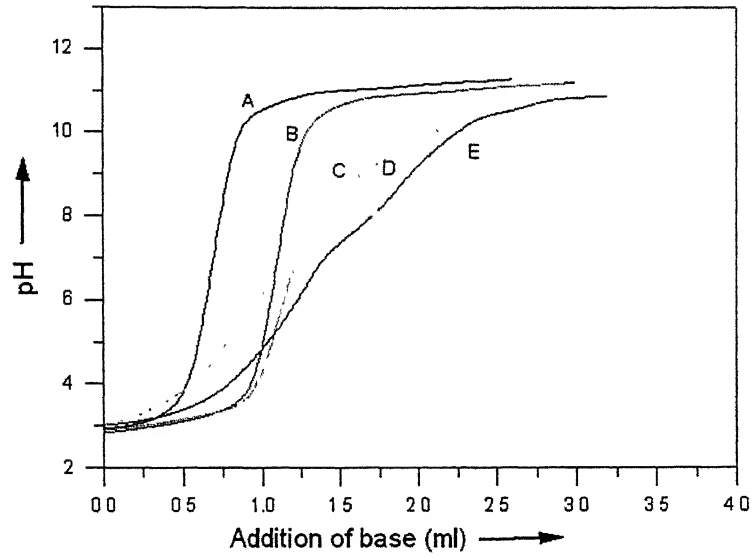



Fig.4.39- Potentiometric titration Curves of 1:1:1:1 Cu(II)-Ni-Proline-Uracil system; (A) Acid (B) Proline (C) Cu(II)-Proline (D) Cu(II)-Proline-Uracil (E) Cu(II)-Ni(II)-Proline-Uracil

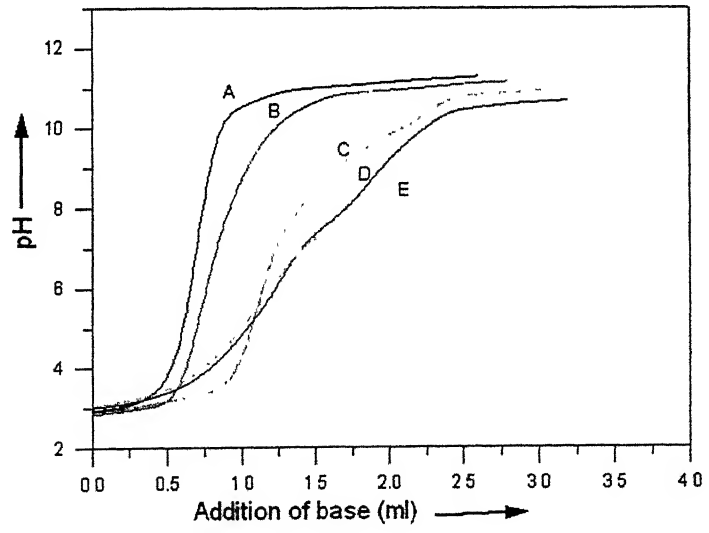



Fig.4.40- Potentiometric titration Curves of 1:1:1:1 Cu(II)-Zn(II)-Proline-Uracil system; (A) Acid (B) Proline (C) Cu(II)-Proline (D) Cu(II)-Proline-Uracil (E) Cu(II)-Zn(II)-Proline-Uracil

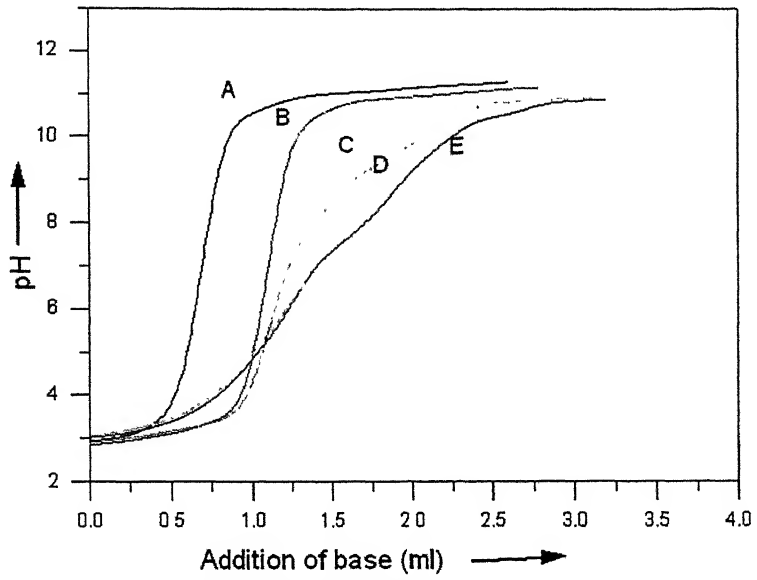



Fig.4.41- Potentiometric titration Curves of 1:1:1:1 Cu(II)-Co(II)-Proline-Uracil system; (A) Acid (B) Proline (C) Cu(II)-Proline (D) Cu(II)-Proline-Uracil (E) Cu(II)-Co(II)-Proline-Uracil

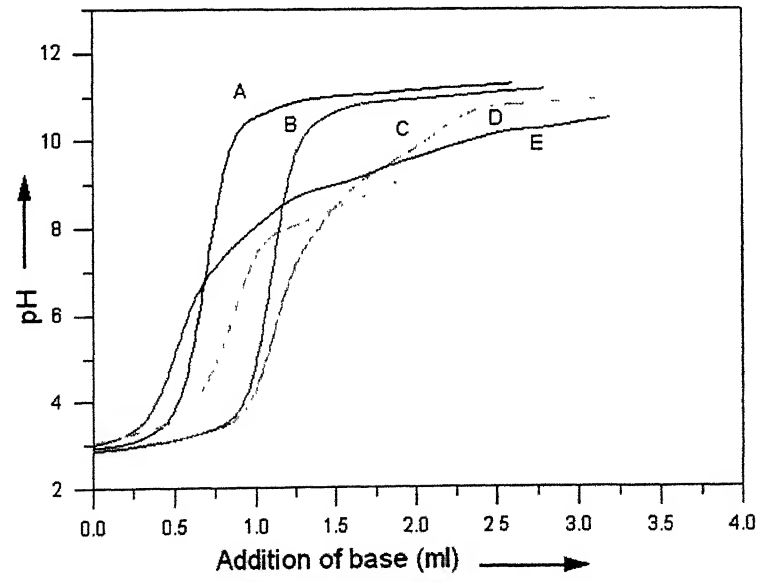



Fig.4.42- Potentiometric titration Curves of 1:1:1:1 Ni(II)-Zn(II)-Proline-Uracil system; (A) Acid (B) Proline (C) Ni(II)-Proline (D) Ni(II)-Proline-Uracil (E) Ni(II)-Zn(II)-Proline-Uracil

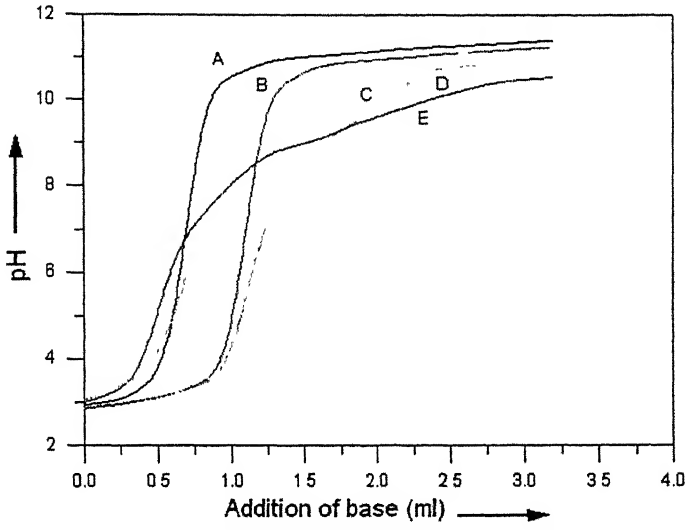



Fig. 4.43- Potentiometric titration Curves of 1:1:1:1 Ni(II)-Co(II)-Proline-Uracil system; (A) Acid (B) Proline (C) Ni(II)-Proline (D) Ni(II)-Proline-Uracil (E) Ni(II)-Co(II)-Proline-Uracil

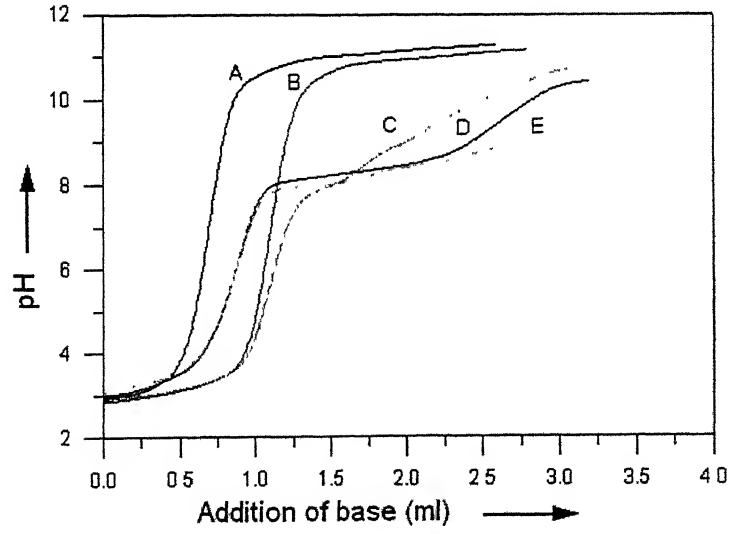



Fig.4.44- Potentiometric titration Curves of 1:1:1:1 Zn(II)-Co(II)- Proline-Uracil system; (A) Acid (B) Proline (C) Zn(II)-Proline (D) Zn(II)-Proline-Uracil (E) Zn(II)-Co(II)-Proline-Uracil

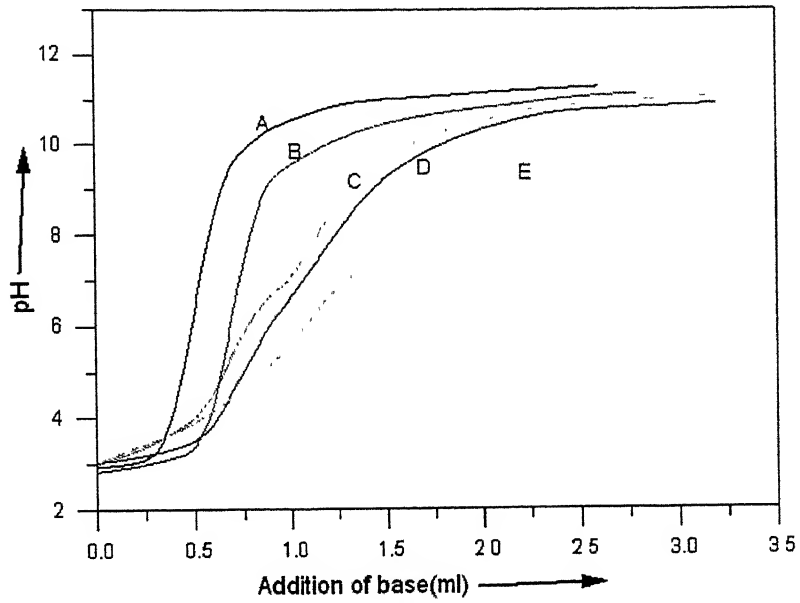



Fig.4.45- Potentiometric titration Curves of 1:1:1:1 Cu(II)-Ni(II) -Valine-Thymine system; (A) Acid (B) Valine (C) Cu(II)-Valine (D) Cu(II)-Valine-Thymine (E) Cu(II)-Ni(II)-Valine-Thymine

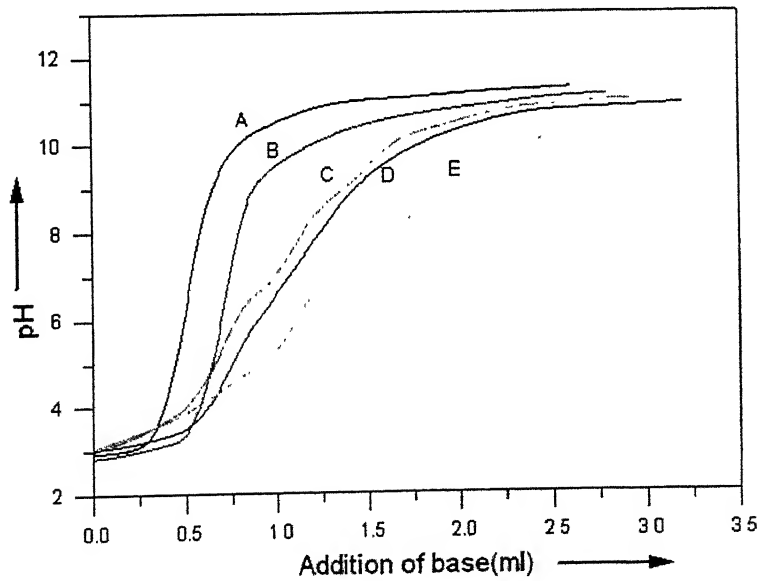



Fig.4.46- Potentiometric titration Curves of 1:1:1:1 Cu(II)-Zn(II) -Valine-Thymine system; (A) Acid (B) Valine (C) Cu(II)-Valine (D) Cu(II)-Valine-Thymine (E) Cu(II)-Zn(II)-Valine-Thymine

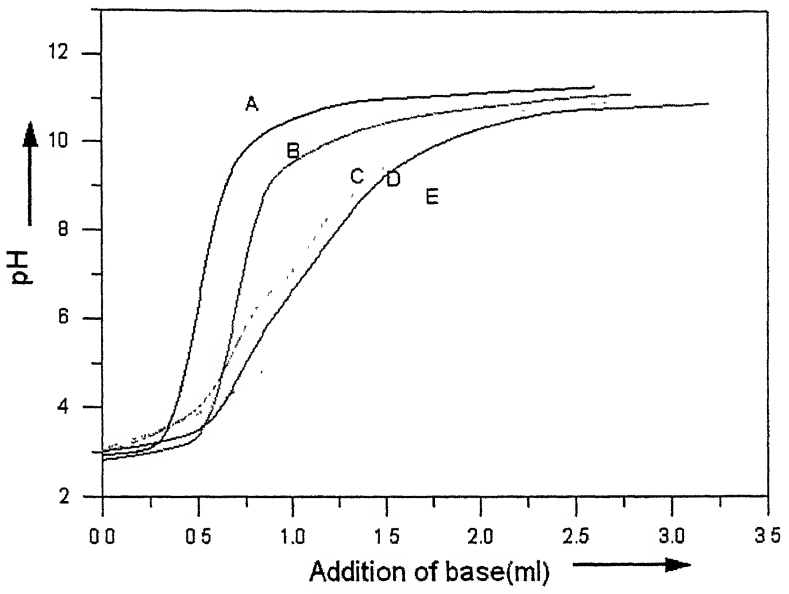



Fig.4.47- Potentiometric titration Curves of 1:1:1:1 Cu(II)-Co(II) -Valine-Thymine system; (A) Acid (B) Valine (C) Cu(II)-Valine (D) Cu(II)-Valine-Thymine (E) Cu(II)-Co(II)-Valine-Thymine

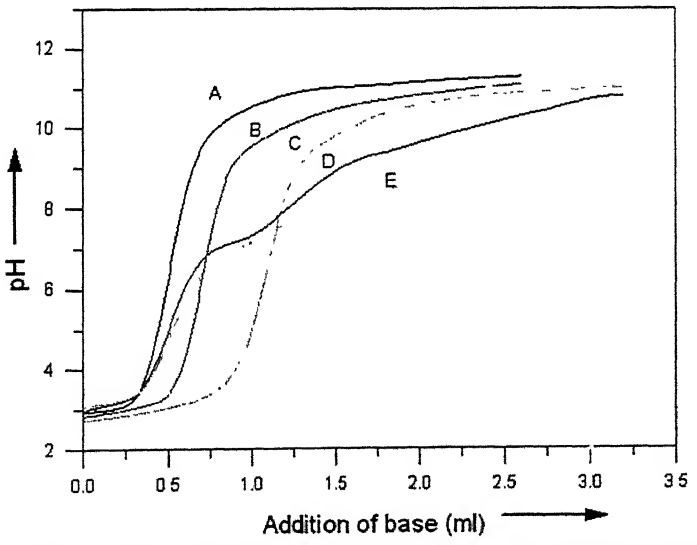



Fig.4.48- Potentiometric titration Curves of 1:1:1:1 Ni(II)-Zn(II) -Valine-Thymine system; (A) Acid (B) Valine (C) Ni(II)-Valine (D) Ni(II)-Valine-Thymine (E) Ni(II)-Zn(II)-Valine-Thymine

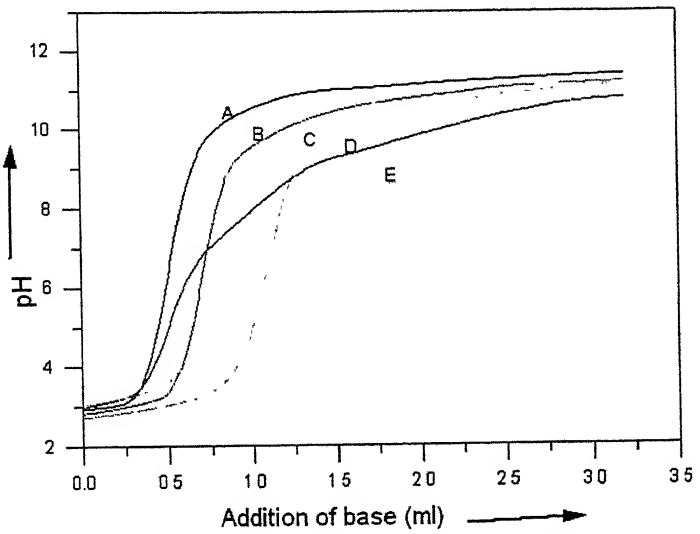



Fig.4.49- Potentiometric titration Curves of 1:1:1:1 Ni(II)-Co(II) -Valine-Thymine system; (A) Acid (B) Valine (C) Ni(II)-Valine (D) Ni(II)-Valine-Thymine (E) Ni(II)-Co(II)-Valine-Thymine

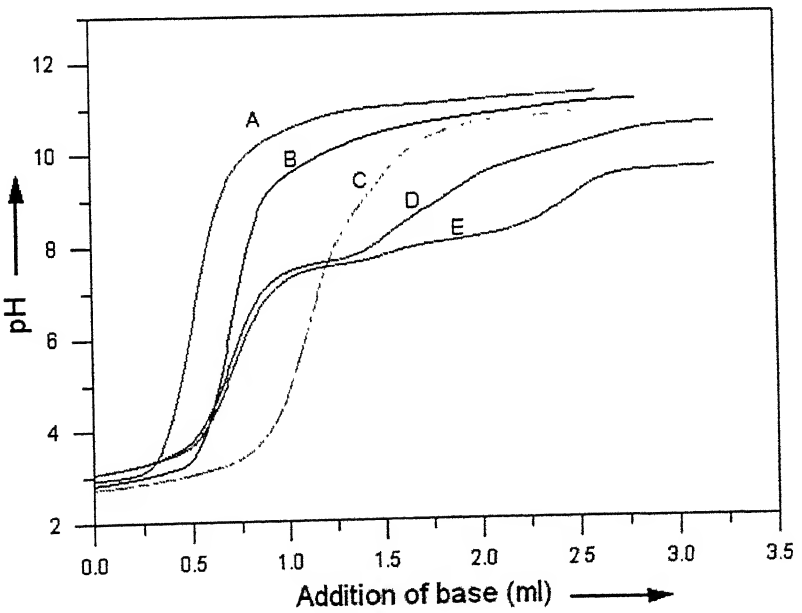



Fig.4.50- Potentiometric titration Curves of 1:1:1:1 Zn(II) -Co(II)- Valine-Thymine system; (A) Acid (B) Valine (C) Zn(II)-Valine (D) Zn(II)-Valine-Thymine (E) Zn(II)-Co(II)-Valine-Thymine

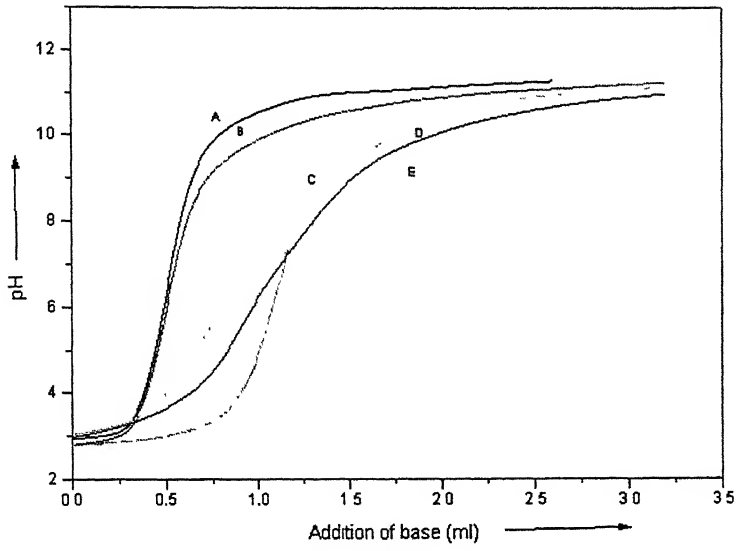



Fig.4.51- Potentiometric titration Curves of 1:1:1:1 Cu(II)-Ni(II) Asparagine-Thymine system; (A) Acid (B)Asparagine (C) Cu(II)-Asparagine (D) Cu(II)-(II)Asparagine-Thymine (E) Cu(II)-Ni(II)-Aspragine-Thymine

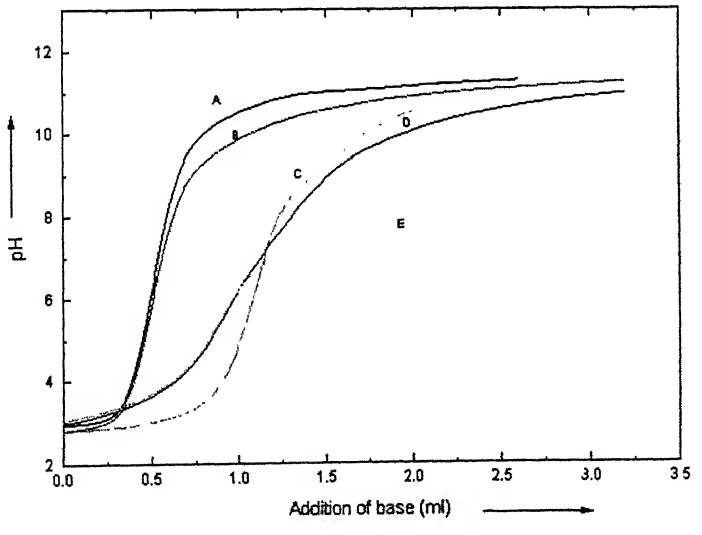



Fig.4.52- Potentiometric titration Curves of 1:1:1:1 Cu(II)-Zn(II) Asparagine-Thymine system; (A) Acid (B)Asparagine (C) Cu(II)-Asparagine (D) Cu(II)-Asparagine-Thymine (E) Cu(II)-Zn(II)-Asparagine-Thymine

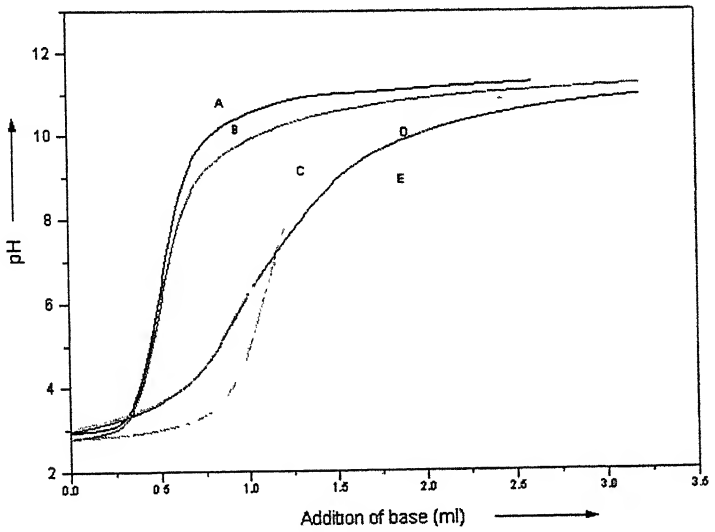



Fig.4.53- Potentiometric titration Curves of 1:1:1:1 Cu(II)-Co(II) Asparagine-Thymine system; (A) Acid (B)Asparagine (C) Cu(II)-Asparagine (D) Cu(II)-Asparagine-Thymine (E) Cu(II)-Co(II)-Asparagine Thymine

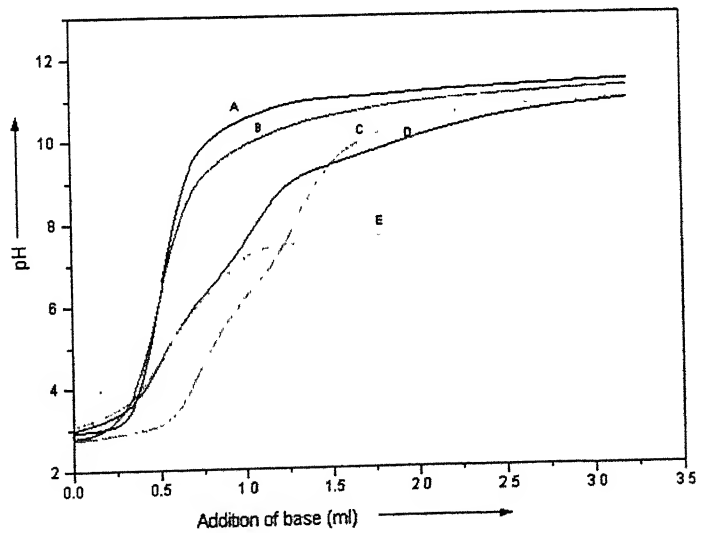



Fig.4.54- Potentiometric titration Curves of 1:1:1:1 Ni(II)- Zn(II)-Asparagine-Thymine system; (A) Acid (B)Asparagine (C) Ni(II)-Asparagine (D) Ni(II)- Asparagine-Thymine (E) Ni(II)-Zn(II)-Asparagine-Thymine

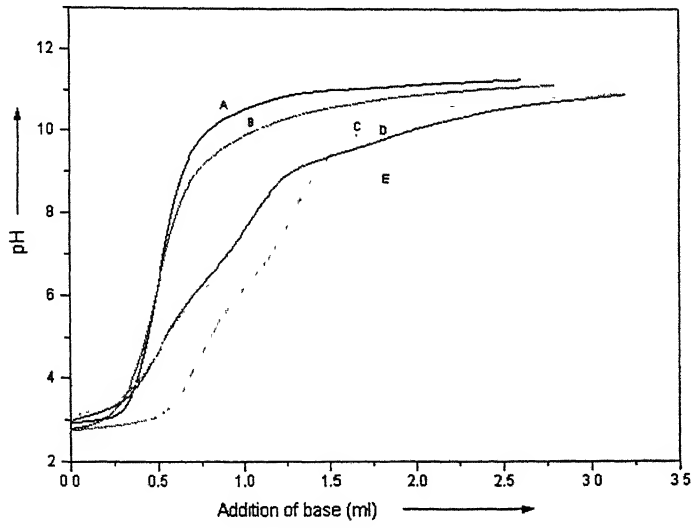



Fig.4.55- Potentiometric titration Curves of 1:1:1:1 Ni(II)-Co(II)-Asparagine-Thymine system; (A) Acid (B)Asparagine (C) Ni(II)-Asparagine (D) Ni(II)-Asparagine-Thymine (E) Ni(II)-Co(II)-Asparagine-Thymine

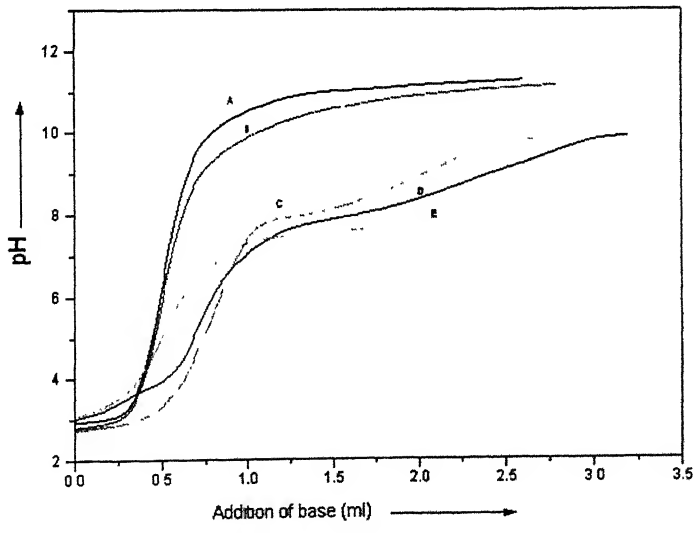



Fig.4.56- Potentiometric titration Curves of 1:1:1:1 Zn(II)-Co(II)-Asparagine-Thymine system; (A) Acid (B)Asparagine (C) Zn(II)-Asparagine (D) Zn(II)-Asparagine-Thymine (E) Zn(II)- Co(II)-Asparagine-Thymine

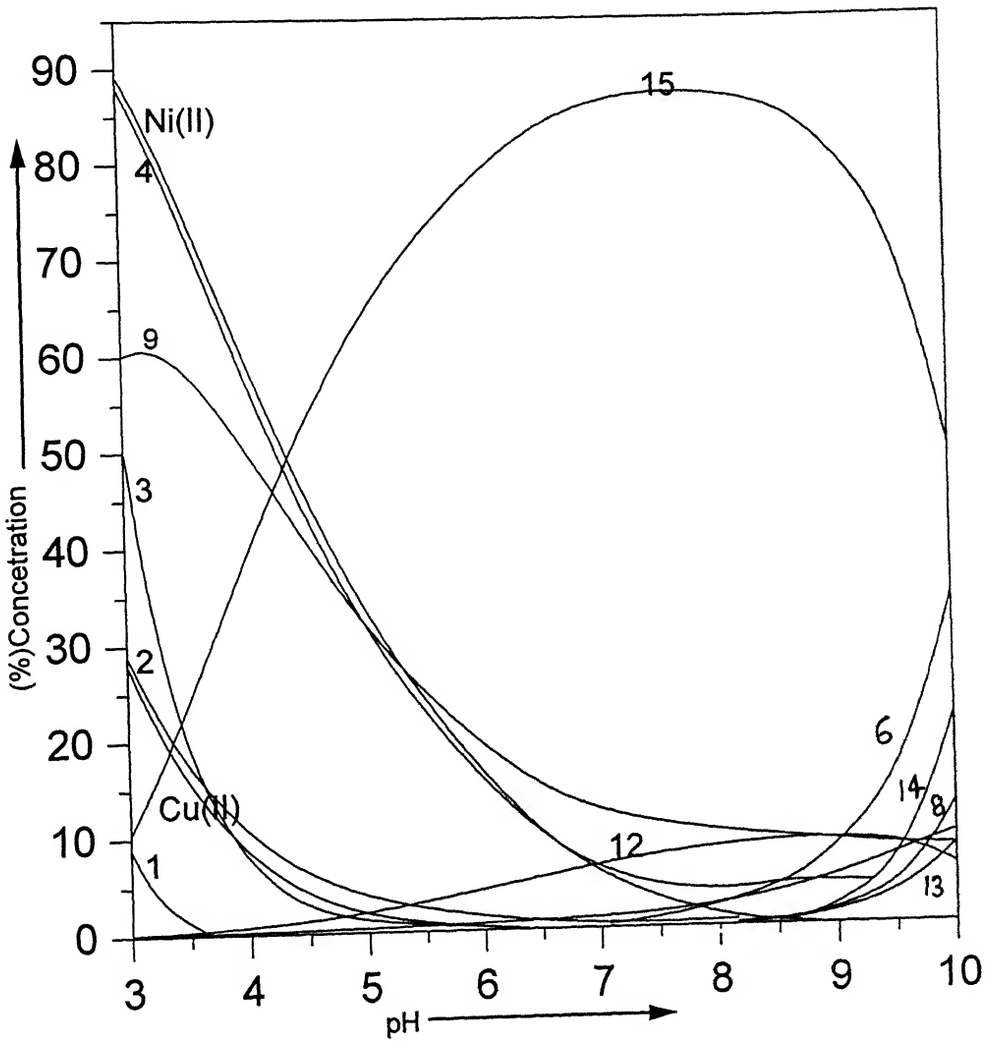



Fig. 4.57- Distribution Curves of 1:1:1:1 Cu(II)-Ni(II)-Lysine-Uracil system; (I) $AH_3$ (2) $AH_2$ (3) AH (4) BH (5) $Cu(OH)^+$ (6) $Cu(OH)_2$ (7) $Ni(OH)^+$ (8) $Ni(OH)_2$ (9) CuA (10) NiA (11) CuB (12) NiB (13) CuAB (14) NiAB (15) CuNiAB

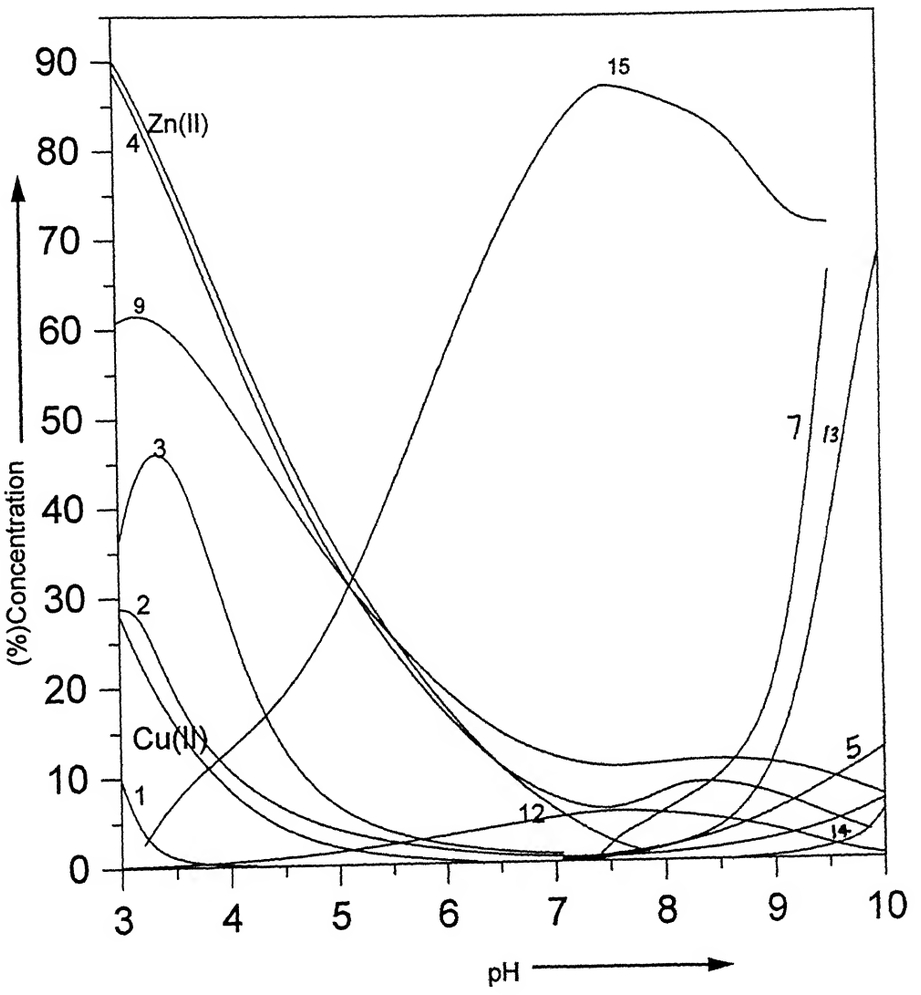



Fig. 4.58- Distribution Curves of 1:1:1:1 Cu(II)-Zn(II)-Lysine-Uracil system;(I) $AH_3$ (2) $AH_2$ (3) AH (4) BH (5) $Cu(OH)^+$ (6) $Cu(OH)_2$ (7) $Zn(OH)^+$ (8) $Zn(OH)_2$ (9) CuA (10) NiA (11) CuB (12) NiB (13) CuAB (14) NiAB (15) CuNiAB

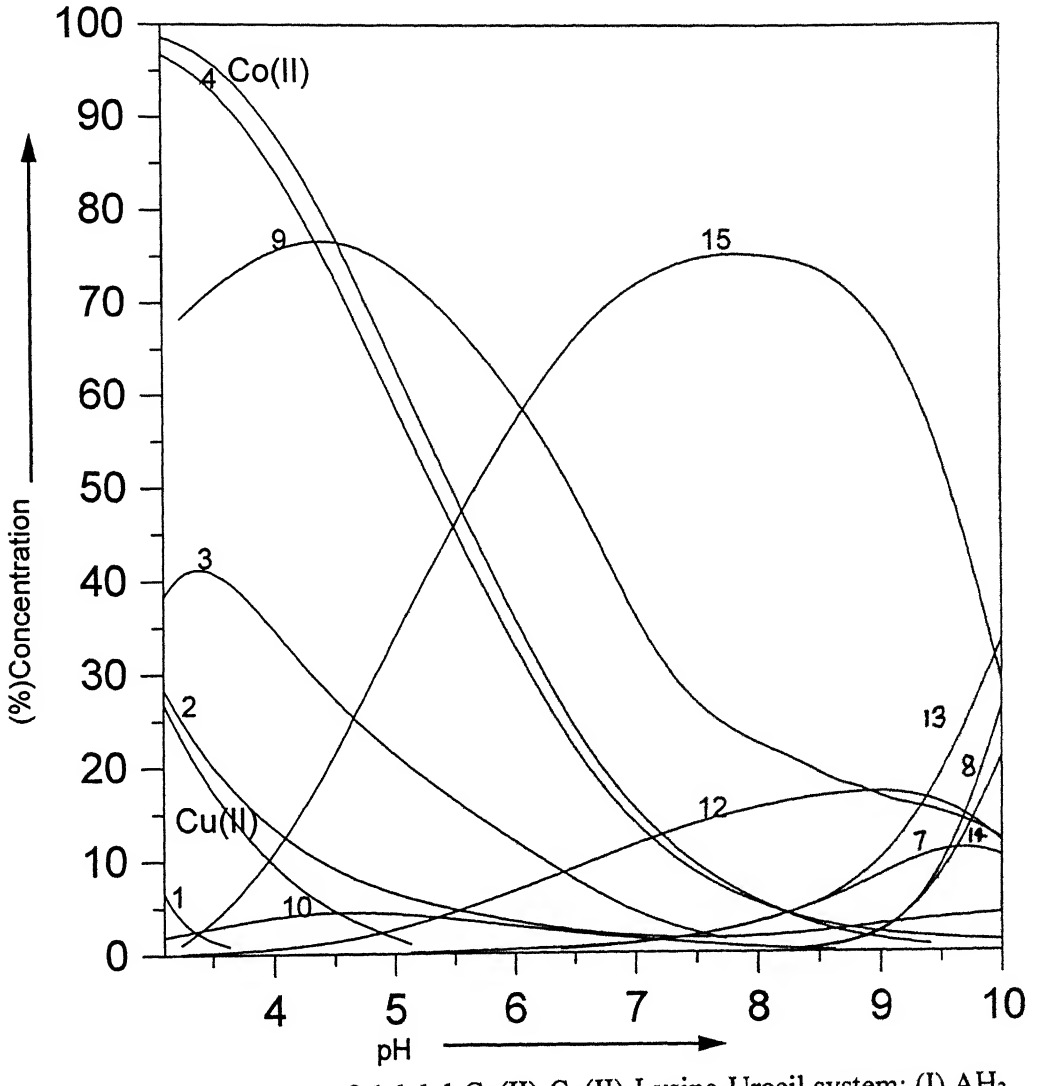



Fig.4.59- Distribution Curves of 1:1:1:1 Cu(II)-Co(II)-Lysine-Uracil system; (I) $AH_3$ (2) $AH_2$ (3) AH (4) BH (5) $Cu(OH)^+$ (6) $Cu(OH)_2$ (7) $Co(OH)^+$ (8) $Co(OH)_2$ (9) CuA (10) CoA (11) CuB (12) CoB (13) CuAB (14) CoAB (15) CuCoAB

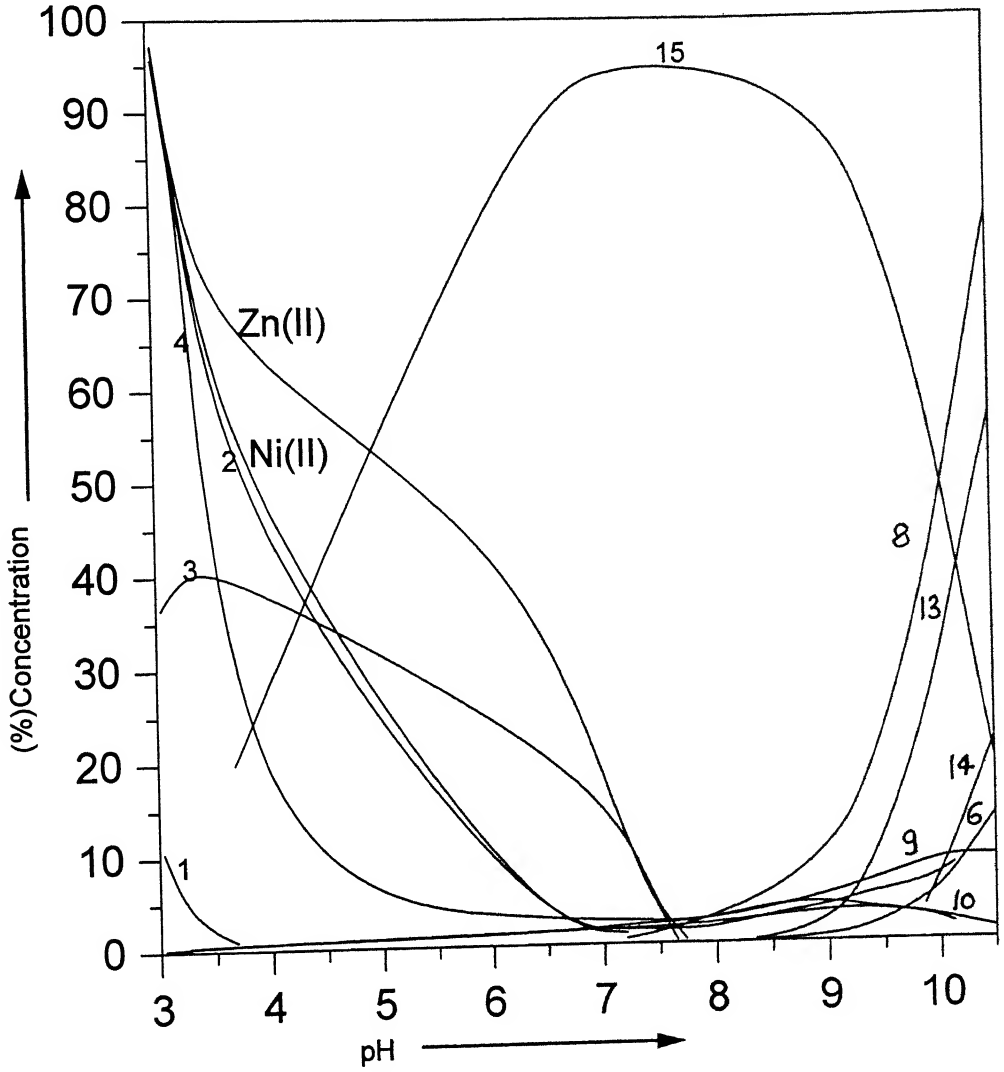



Fig.4.60-Distribution Curves of 1:1:1:1 Ni(II)-Zn(II)-Lysine-Uracil system; (I) $AH_3$ (2) $AH_2$ (3) AH (4) BH (5) $Ni(OH)^+$ (6) $Ni(OH)_2$ (7) $Zn(OH)^+$ (8) $Zn(OH)_2$ (9) NiA (10) NiB (11) ZnA (12) ZnB (13) NiAB (14)ZnAB (15) NiZnAB

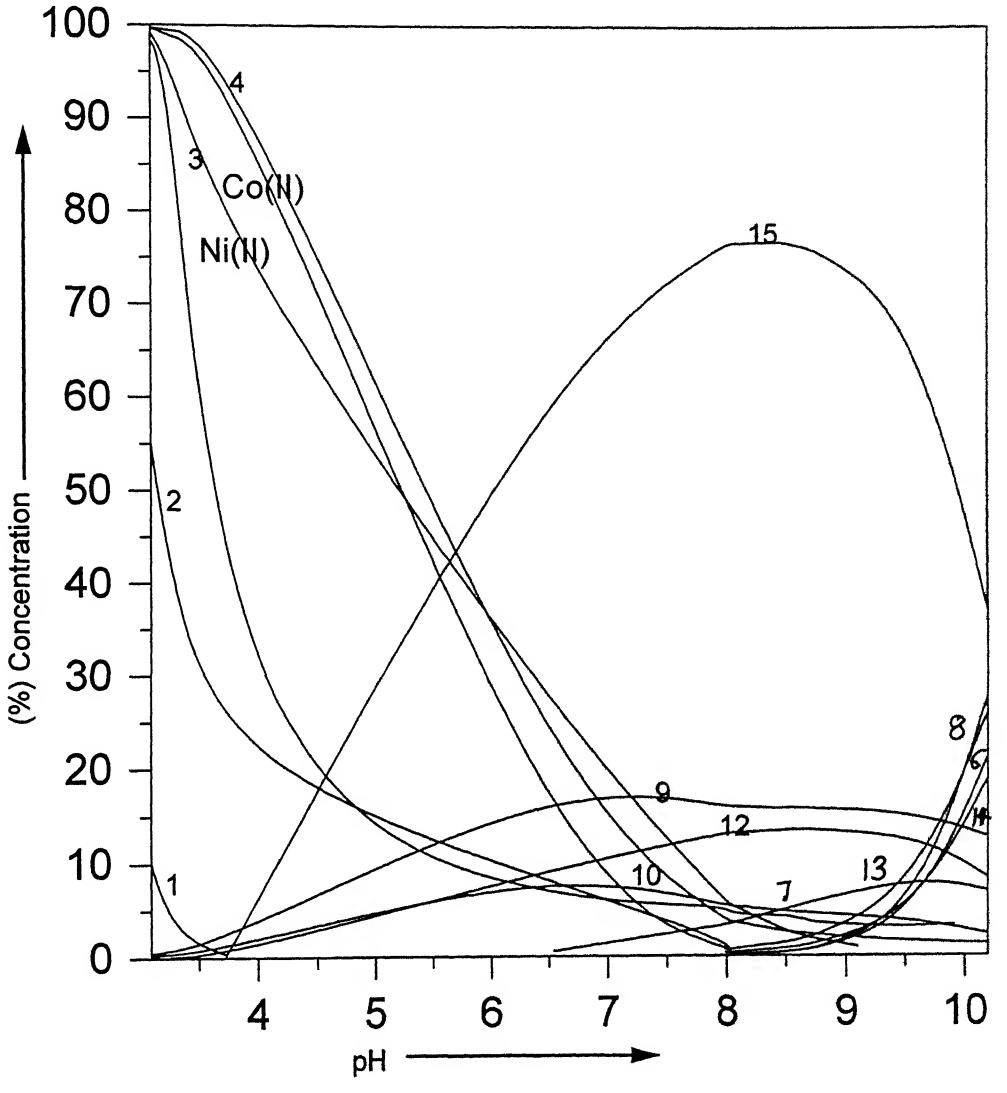



Fig. 4.61-Distribution Curves of 1:1:1:1 Ni(II)-Co(II)-Lysine-Uracil system;(I) $AH_3$ (2) $AH_2$ (3) AH (4) BH (5) $Ni(OH)^+$ (6) $Ni(OH)_2$ (7) $Co(OH)^+$ (8) $Co(OH)_2$ (9) NiA (10) NiB (11)CoA (12) CoB (13) NiAB (14)CoAB (15) NiCoAB

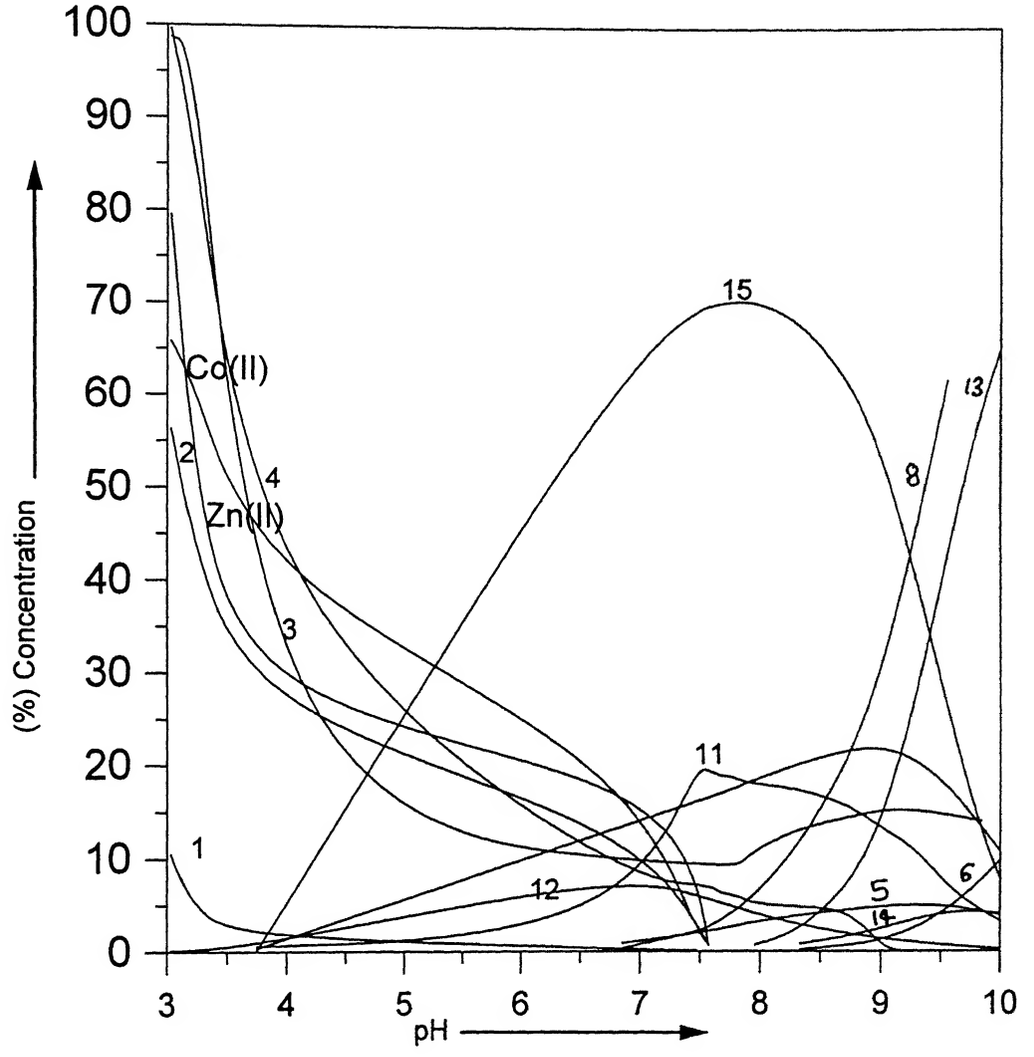



Fig.4.62- Distribution Curves of 1:1:1:1 Zn(II)-Co(II)- Lysine-Uracil system; (I) $AH_3$ (2) $AH_2$ (3) AH (4) BH (5) $Zn(OH)^+$ (6) $Zn(OH)_2$ (7) $Co(OH)^+$ (8) $Co(OH)_2$ (9) ZnA (10) ZnB (11) CoA (12) CoB (13) ZnAB (14) CoAB (15) ZnCoAB

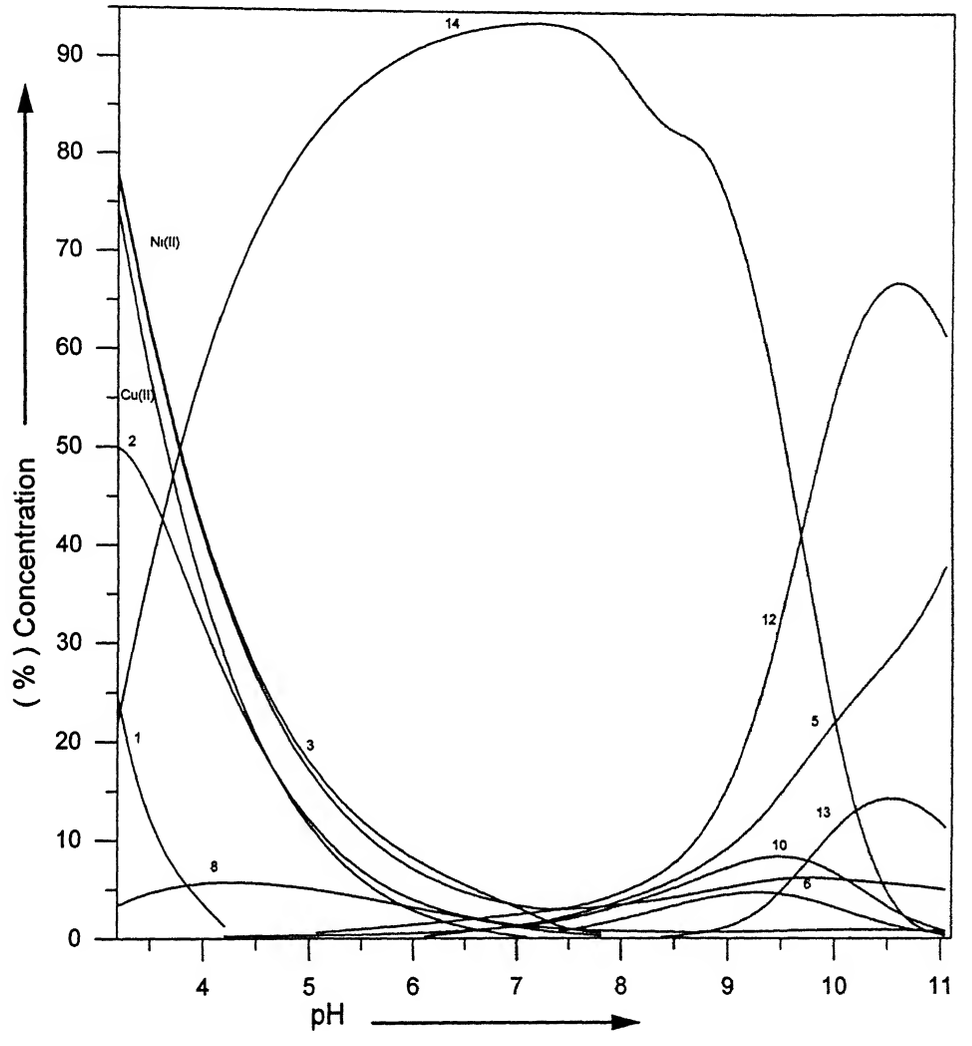



Fig.4.63- Distribution Curves of 1:1:1:1 Cu(II)-Ni(II)-Proine-Uracil system; (I) $AH_2$ (2) AH (3) BH (4) $Cu(OH)^+$ (5) $Cu(OH)_2$ (6) $Ni(OH)^+$ (7) $Ni(OH)_2$ (8) CuA (9) CuB (10) NiA (11) NiB (12) CuAB (13) NiAB (14) CuNiAB

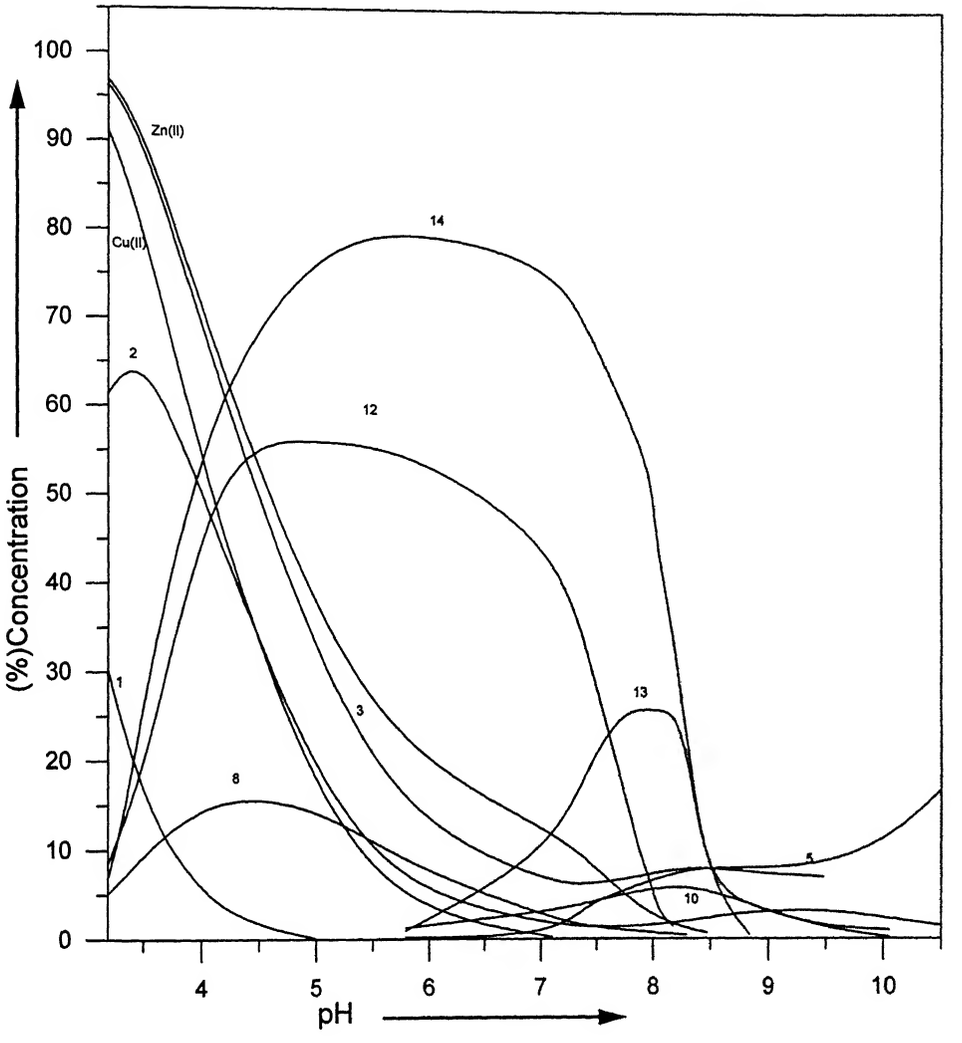



Fig.4.64- Distribution Curves of 1:1:1:1 Cu(II)-Zn(II)-Proine-Uracil system; (I) $AH_2$ (2) AH (3) BH (4) $Cu(OH)^+$ (5) $Cu(OH)_2$ (6) $Zn(OH)^+$ (7) $Zn(OH)_2$ (8) CuA (9) CuB (10) ZnA (11) ZnB (12) CuAB (13) ZnAB (14) CuZnAB

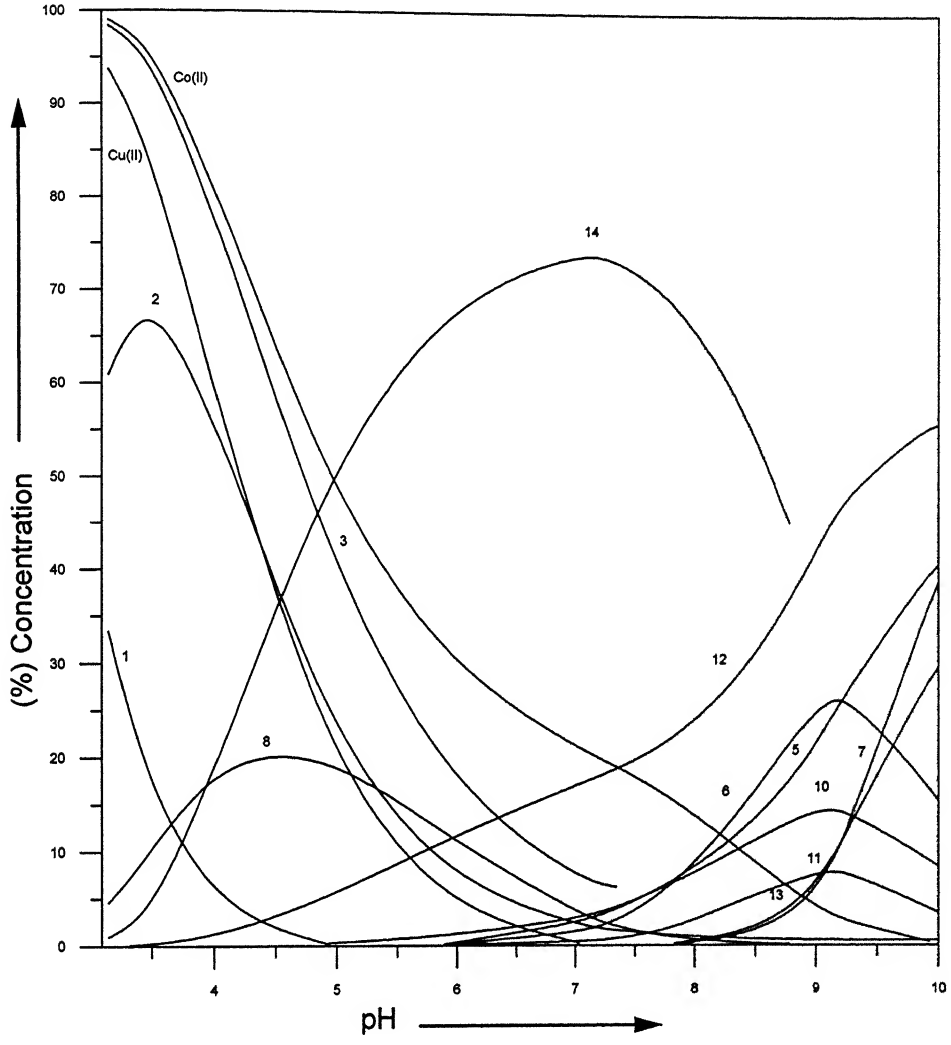



Fig.4.65- Distribution Curves of 1:1:1:1 Cu(II)-Co(II)-Proine-Uracil system; (I) $AH_2$ (2) AH (3) BH (4) $Cu(OH)^+$ (5) $Cu(OH)_2$ (6) $Co(OH)^+$ (7) $Co(OH)_2$ (8) CuA (9) CuB (10) CoA (11) CoB (12) CuAB (13) CoAB (14) CuCoAB

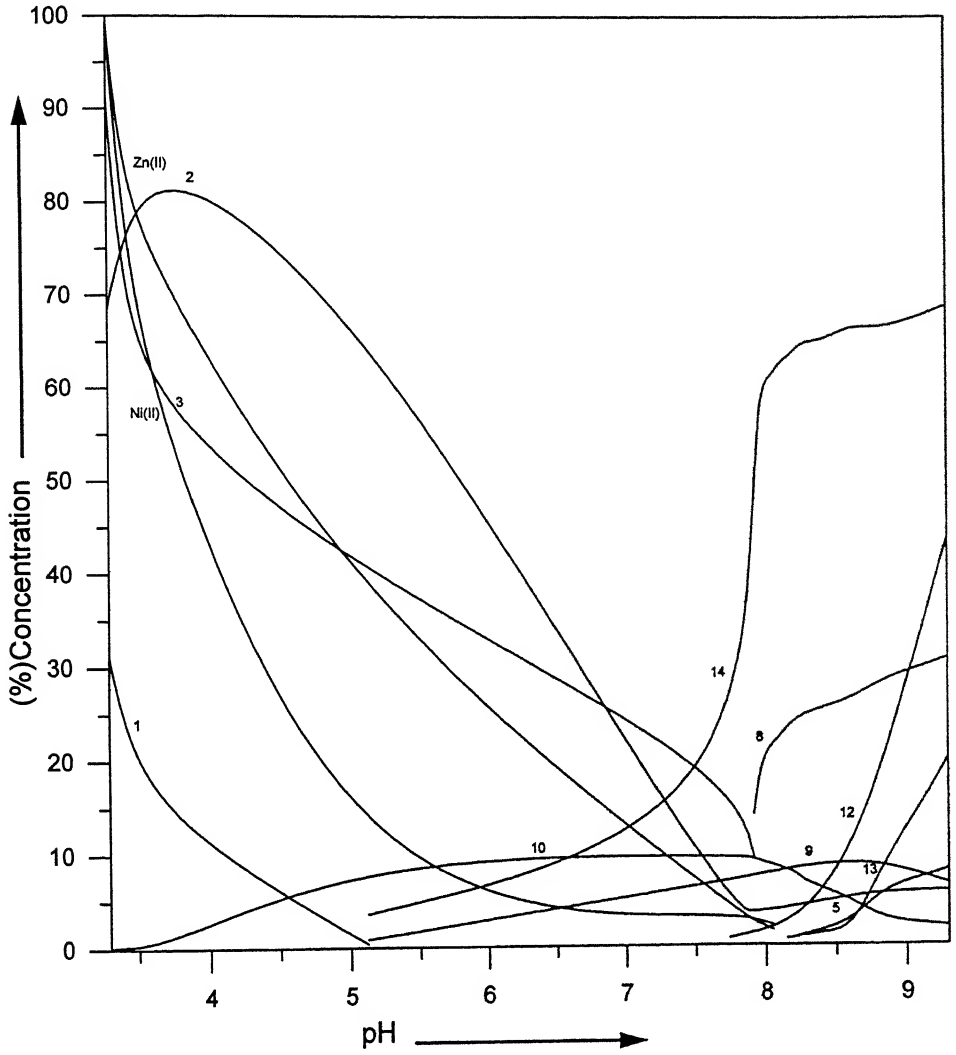



Fig.4.66- Distribution Curves of 1:1:1:1 Ni(II)-Zn(II)-Proine-Uracil system; (I) $AH_2$ (2) AH (3) BH (4) $Ni(OH)^+$ (5) $Ni(OH)_2$ (6) $Zn(OH)^+$ (7) $Zn(OH)_2$ (8) NiA (9) NiB (10) ZnA (11) ZnB (12) NiAB (13) ZnAB (14) NiZnAB

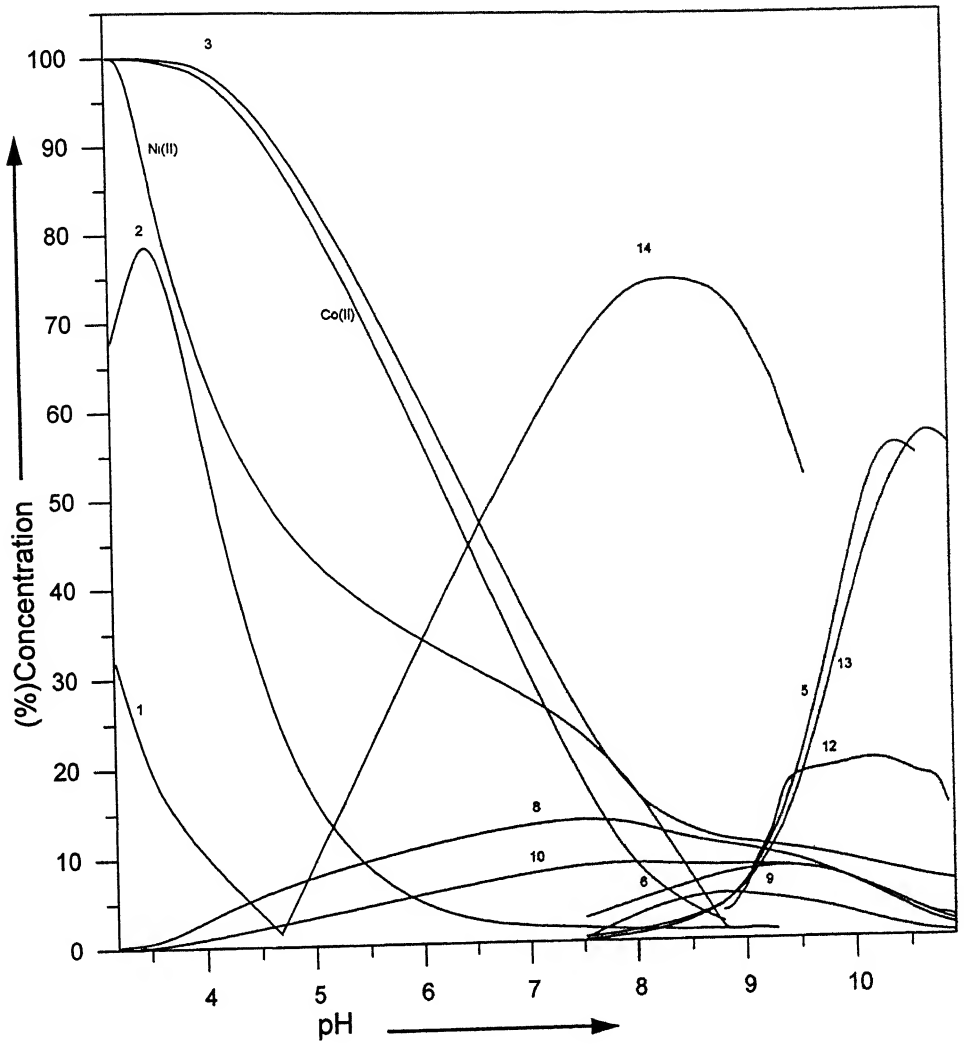



Fig.4.67- Distribution Curves of 1:1:1:1 Ni(II)-Co(II)-Proine-Uracil system; (I) $AH_2$ (2) AH (3) BH (4) $Ni(OH)^+$ (5) $Ni(OH)_2$ (6) $Co(OH)^+$ (7) $Co(OH)_2$ (8) NiA (9) NiB (10) CoA (11) CoB (12) NiAB (13) CoAB (14) NiCoAB

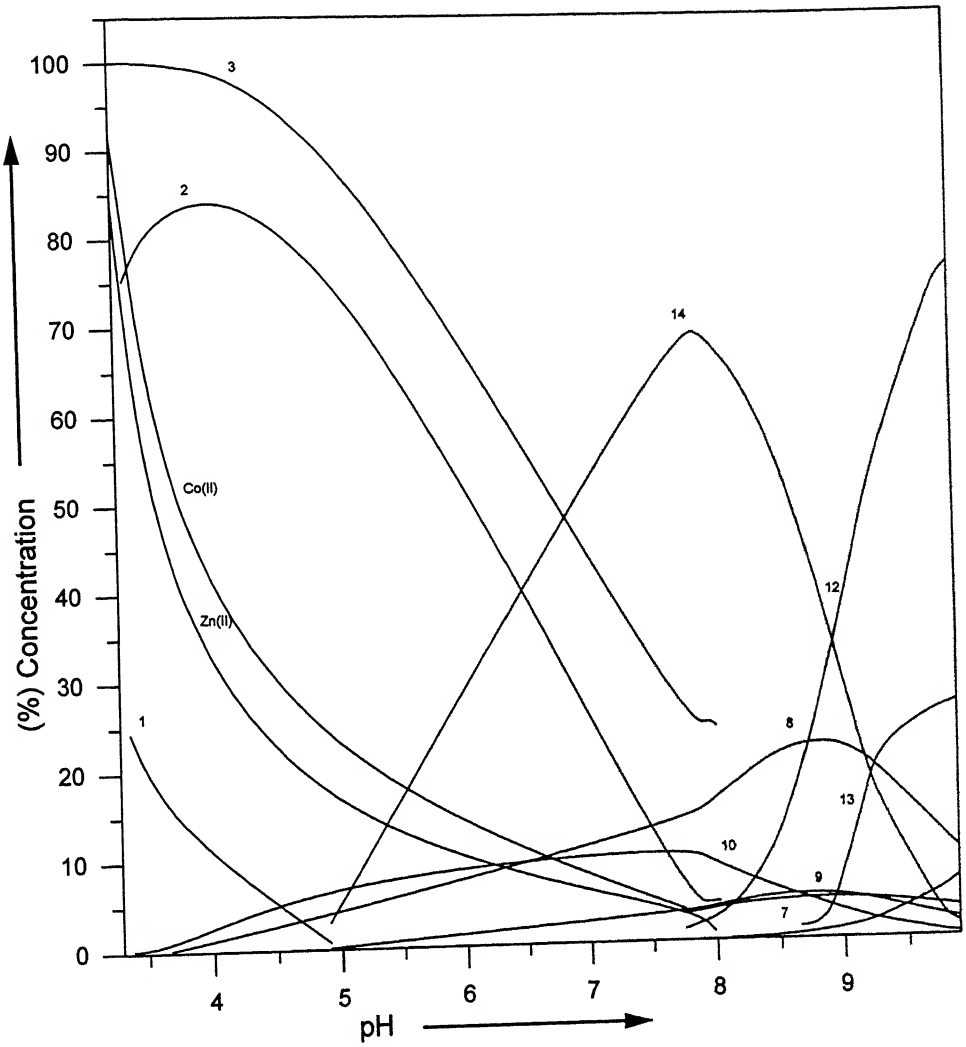



Fig.4.68- Distribution Curves of 1:1:1:1 Zn(II)-Co(II)- Proine-Uracil system; (I) $AH_2$ (2) AH (3) BH (4) $Zn(OH)^+$ (5) $Zn(OH)_2$ (6) $Co(OH)^+$ (7) $Co(OH)_2$ (8) ZnA (9) ZnB (10) CoA (11) CoB (12) ZnAB (13) CoAB (14) ZnCoAB

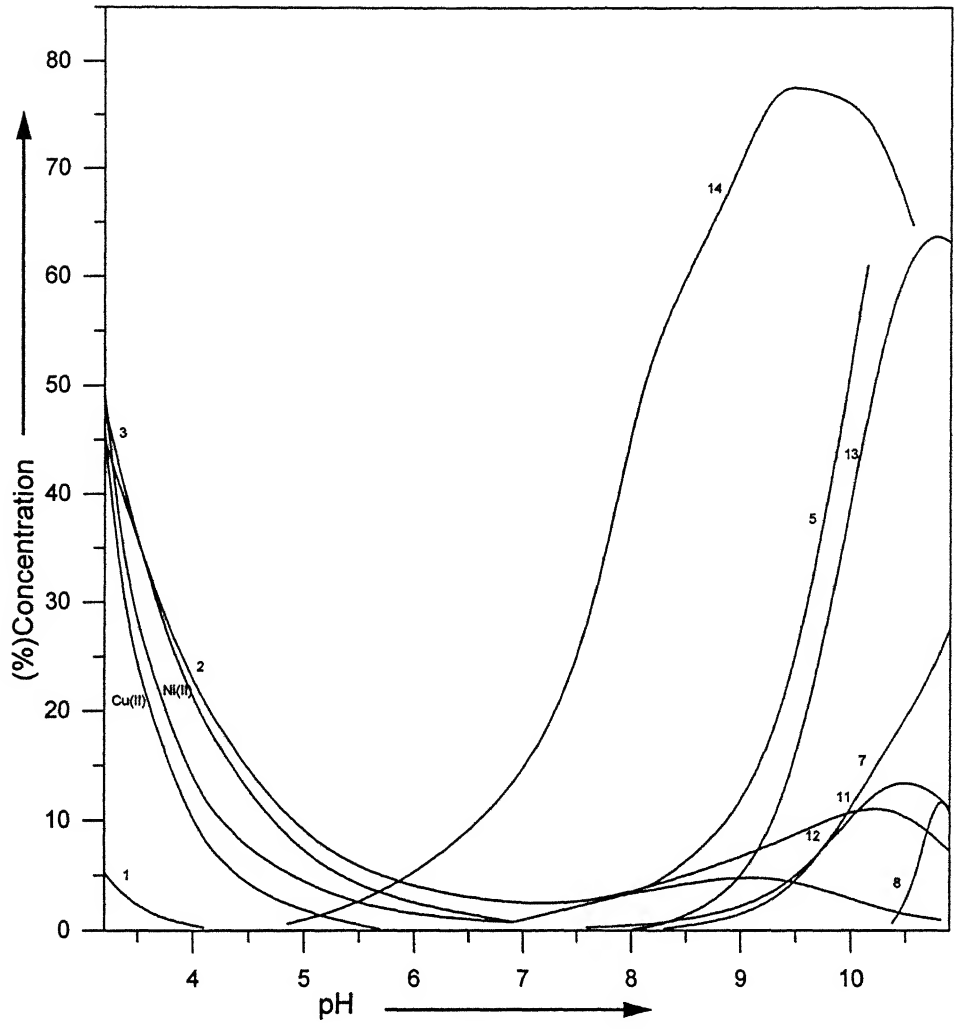



Fig.4.69- Distribution Curves of 1:1:1:1 Cu(II)-Ni(II)-Valine-Thymine system; (I) $AH_2$ (2) AH (3) BH (4) $Cu(OH)^+$ (5) $Cu(OH)_2$ (6) $Ni(OH)^+$ (7) $Ni(OH)_2$ (8) CuA (9) CuB (10) NiA (11) NiB (12) CuAB (13) NiAB (14) CuNiAB

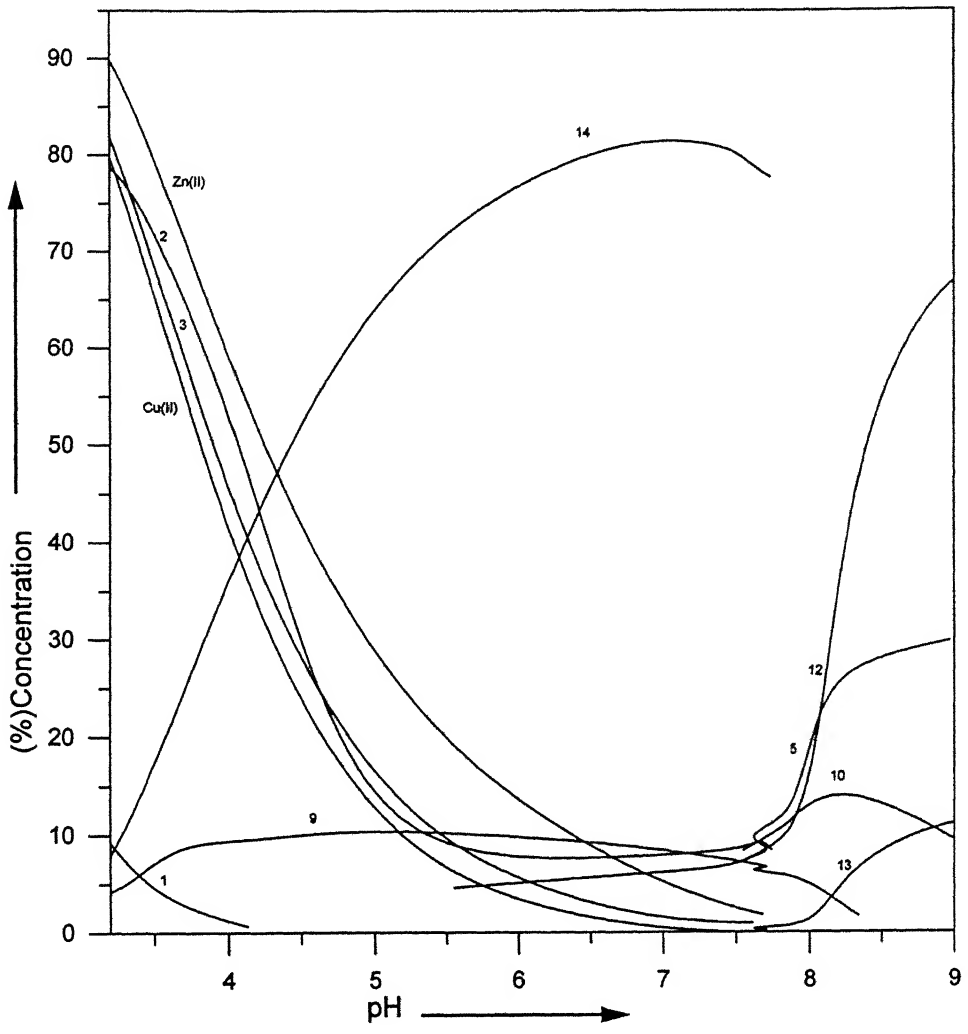



Fig.4.70- Distribution Curves of 1:1:1:1 Cu(II)-Zn(II)-Valine-Thymine system; (I) $AH_2$ (2) AH (3) BH (4) $Cu(OH)^+$ (5) $Cu(OH)_2$ (6) $Zn(OH)^+$ (7) $Zn(OH)_2$ (8) CuA (9) CuB (10) ZnA (11) ZnB (12) CuAB (13) ZnAB (14) CuZnAB

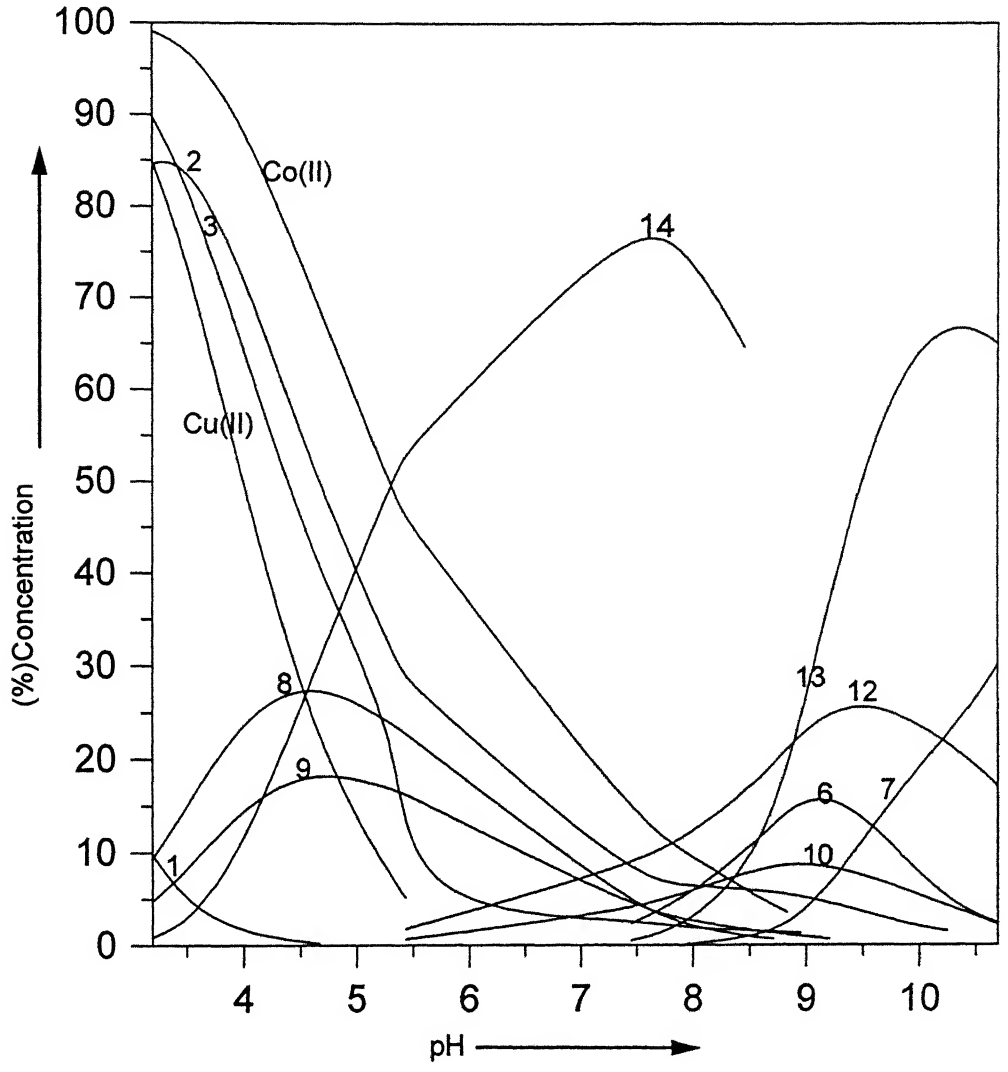



Fig.4.71- Distribution Curves of 1:1:1:1 Cu(II)-Co(II)-Valine-Thymine system; (I) $AH_2$ (2) AH (3) BH (4) $Cu(OH)^+$ (5) $Cu(OH)_2$ (6) $Co(OH)^+$ (7) $Co(OH)_2$ (8) CuA (9) CuB (10) CoA (11) CoB (12) CuAB (13) CoAB (14) CuCoAB

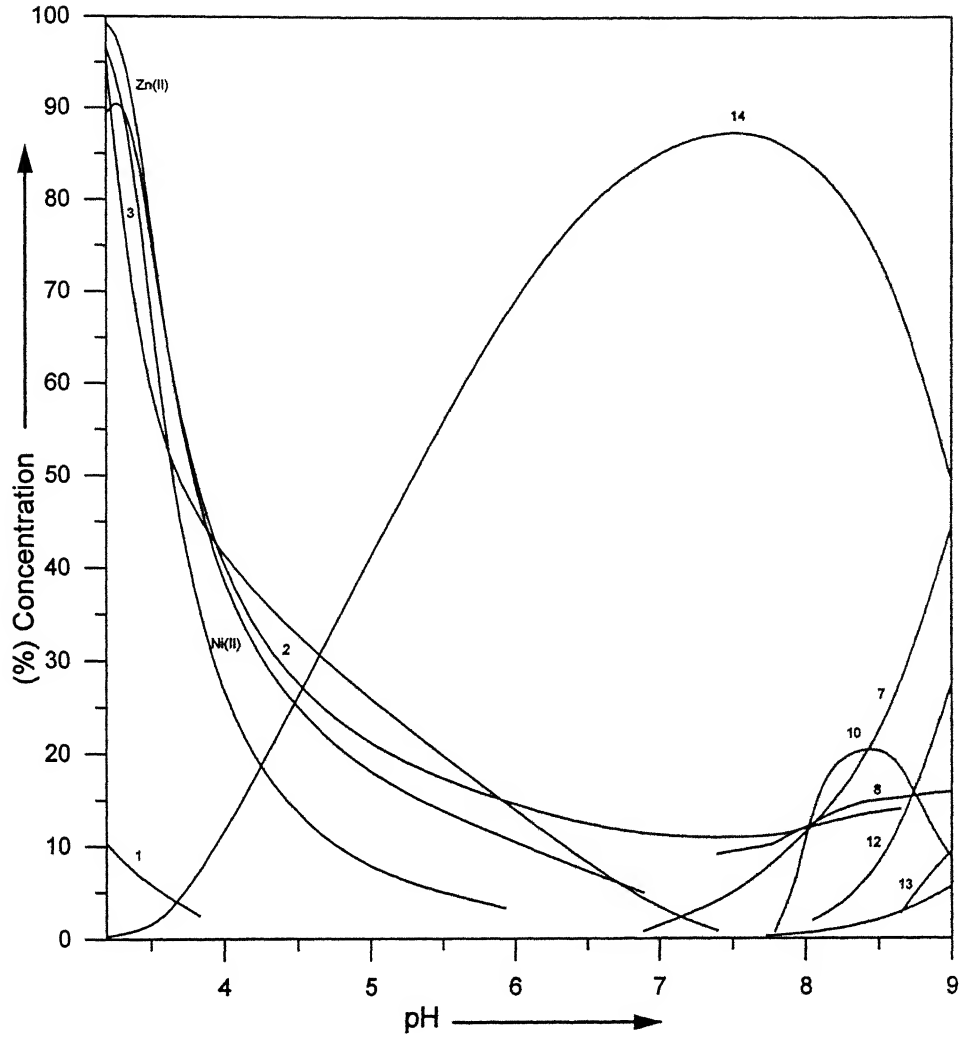



Fig.4.72- Distribution Curves of 1:1:1:1 Ni(II)-Zn(II)-Valine-Thymine system; (I) $AH_2$ (2) AH (3) BH (4) $Ni(OH)^+$ (5) $Ni(OH)_2$ (6) $Zn(OH)^+$ (7) $Zn(OH)_2$ (8) NiA (9) NiB (10) ZnA (11) ZnB (12) NiAB (13) ZnAB (14) NiZnAB

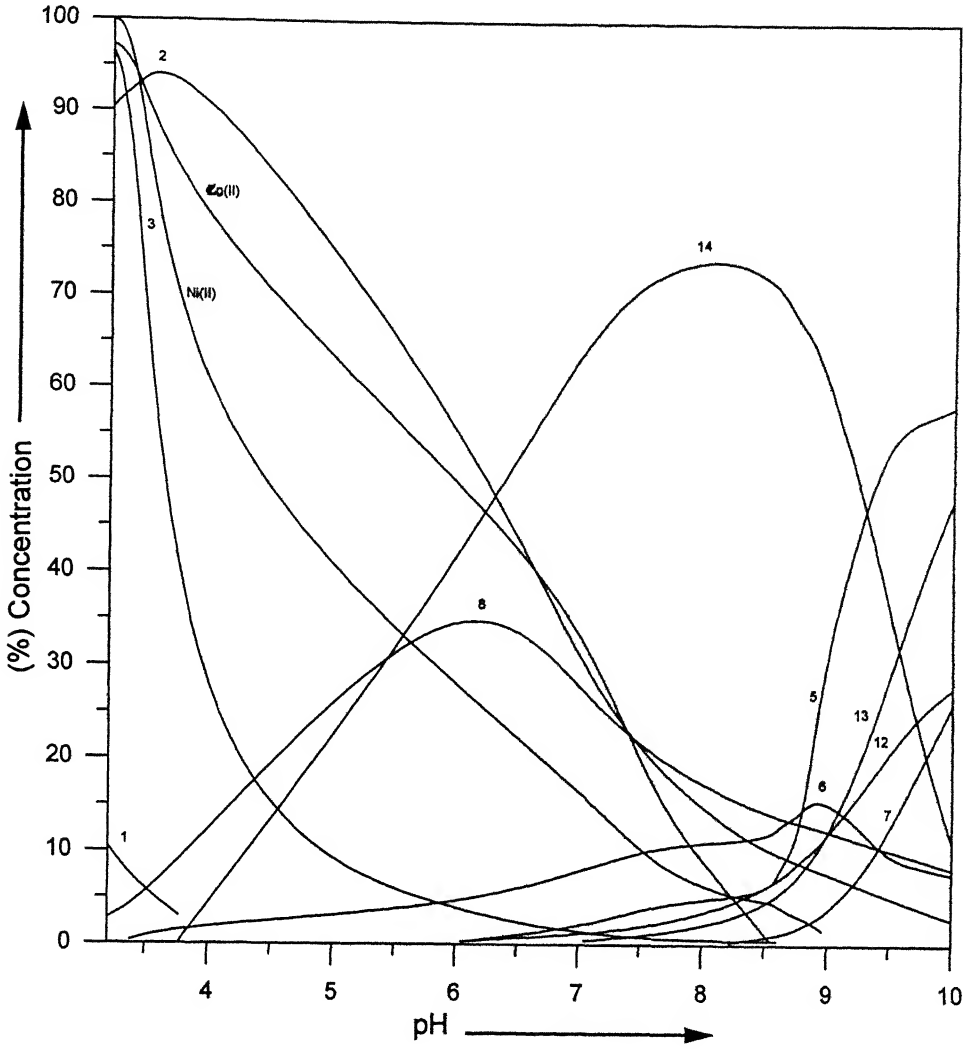



Fig.4.73- Distribution Curves of 1:1:1:1 Ni(II)-Co(II)-Valine-Thymine system; (I) $AH_2$ (2) AH (3) BH (4) $Ni(OH)^+$ (5) $Ni(OH)_2$ (6) $Co(OH)^+$ (7) $Co(OH)_2$ (8) NiA (9) NiB (10) CoA (11) CoB (12) NiAB (13) CoAB (14) NiCoAB

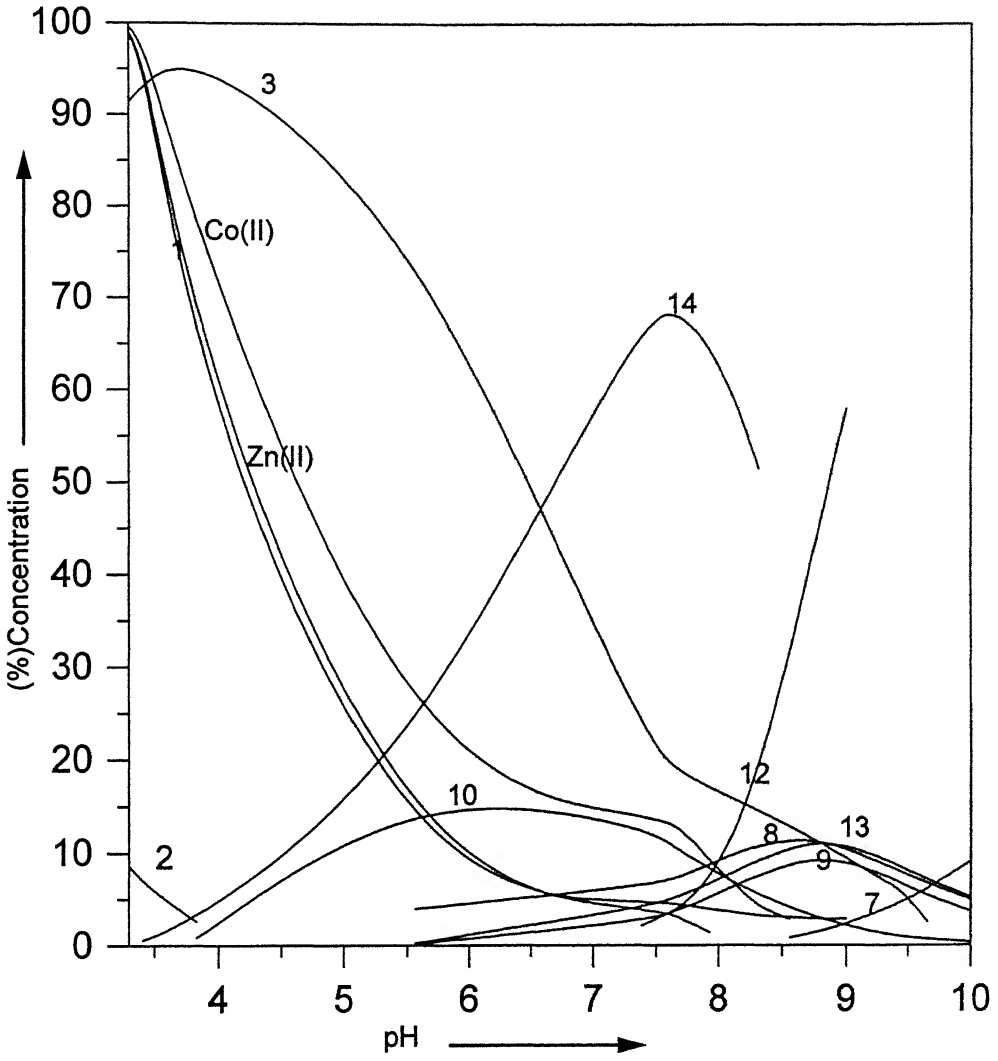



Fig.4.74- Distribution Curves of 1:1:1:1 Zn(II)-Co(II)- Valine-Thymine system; (I) $AH_2$ (2) AH (3) BH (4) $Co(OH)^+$ (5) $Co(OH)_2$ (6) $Zn(OH)^+$ (7) $Zn(OH)_2$ (8) ZnA (9) ZnB (10)CoA (11) CoB (12) ZnAB (13) CoAB (14) ZnCoAB

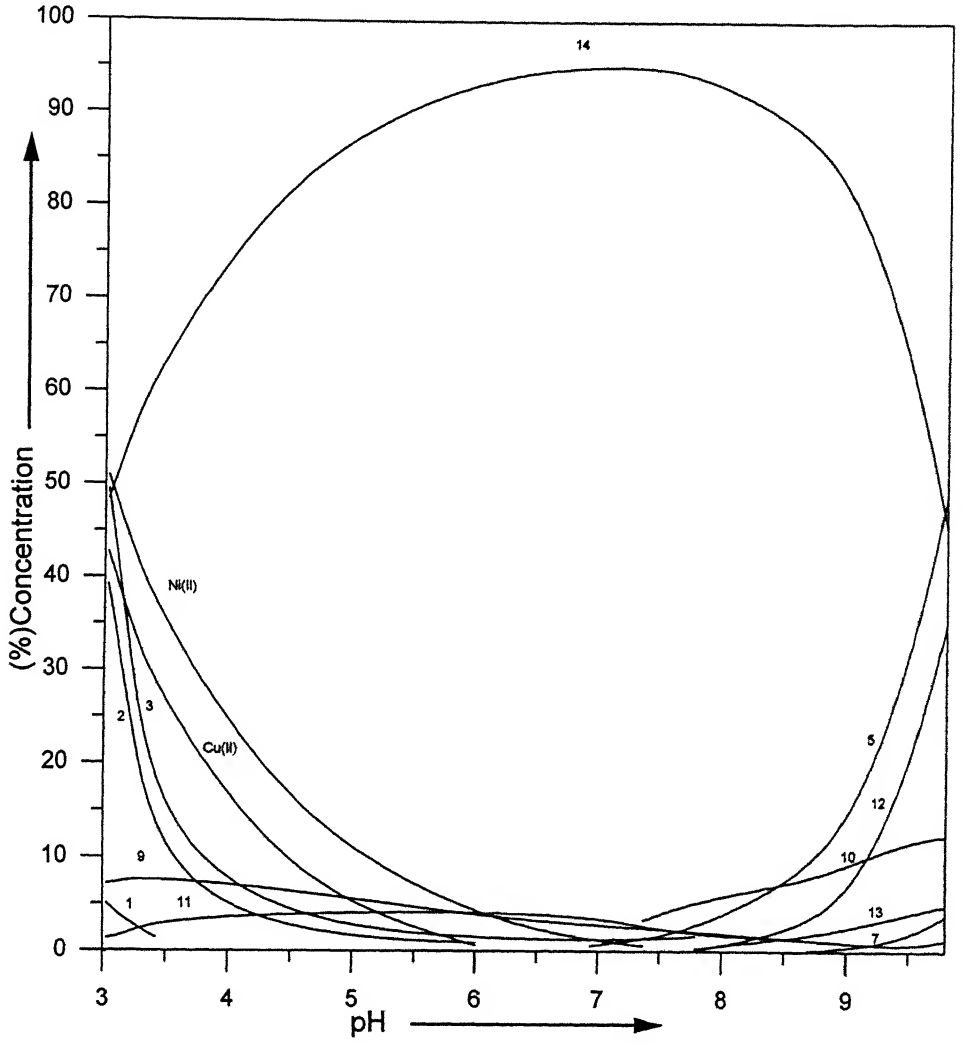



Fig.4.75- Distribution Curves of 1:1:1:1 Cu(II)-Ni(II)-Asparagine-Thymine system;(I)$AH_2$ (2) AH(3) BH (4) $Cu(OH)^+$ (5) $Cu(OH)_2$ (6) $Ni(OH)^+$ (7) $Ni(OH)_2$ (8) CuA (9) CuB (10) NiA (11) NiB (12) CuAB (13) NiAB (14) CuNiAB

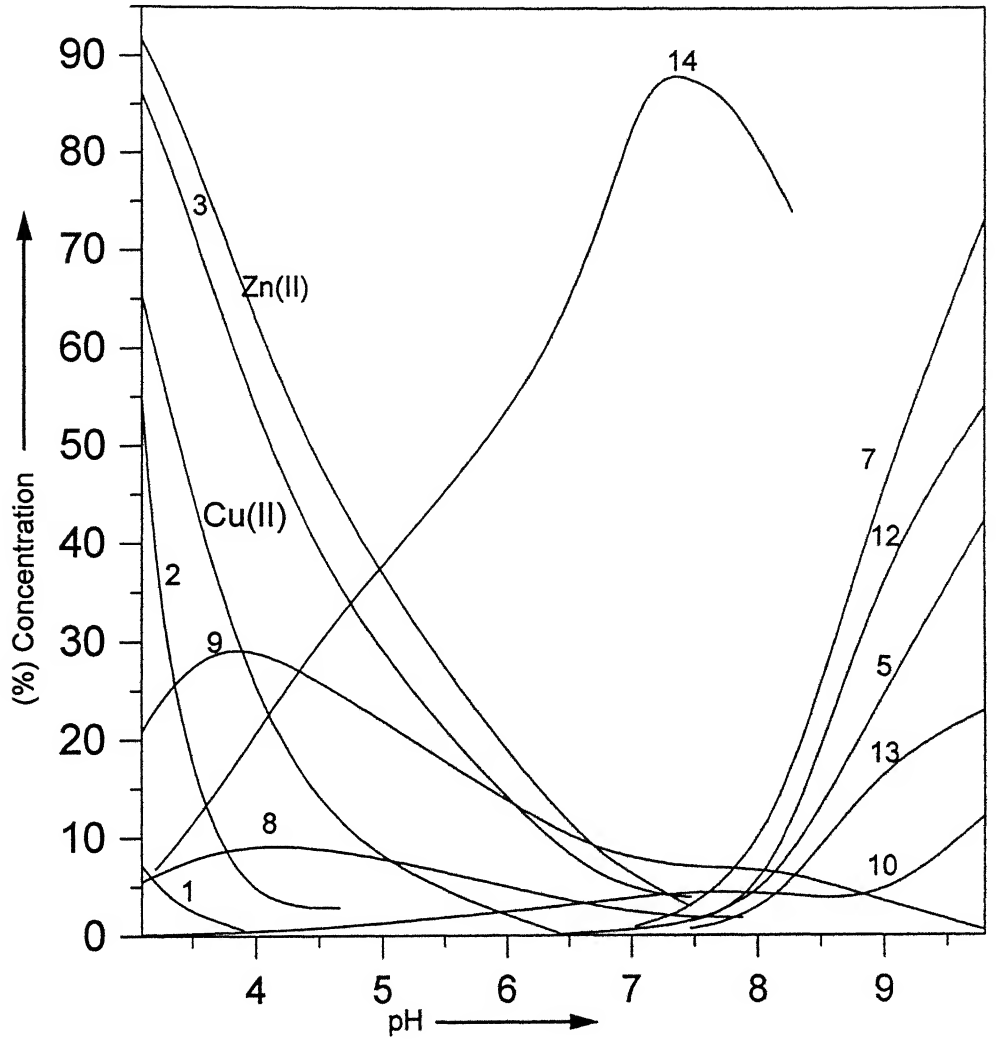



Fig.4.76- Distribution Curves of 1:1:1:1 Cu(II)-Zn(II)-Asparagine-Thymine system; (I) $AH_2$ (2) AH (3) BH (4) $Cu(OH)^+$ (5) $Cu(OH)_2$ (6) $Zn(OH)^+$ (7) $Zn(OH)_2$ (8) CuA (9) CuB (10) ZnA (11) ZnB (12) CuAB (13) ZnAB (14) CuZnAB

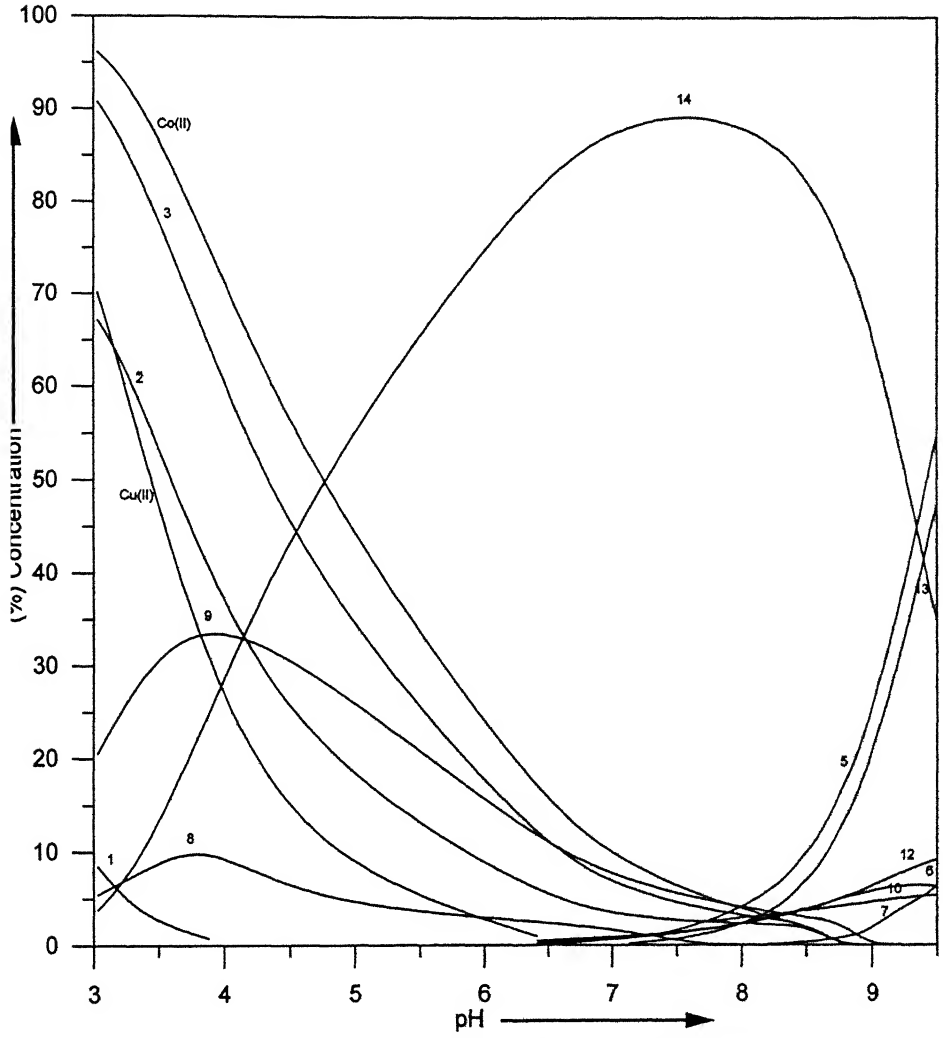



Fig.4.77-Distribution Curves of 1:1:1:1 Cu(II)-Co(II)-Asparagine-Thymine system; (I) $AH_2$ (2) AH(3) BH (4) $Cu(OH)^+$ (5) $Cu(OH)_2$ (6) $Co(OH)^+$ (7) $Co(OH)_2$ (8) CuA (9) CuB (10) CoA (11) CoB (12) CuAB (13) CoAB (14) CuCoAB

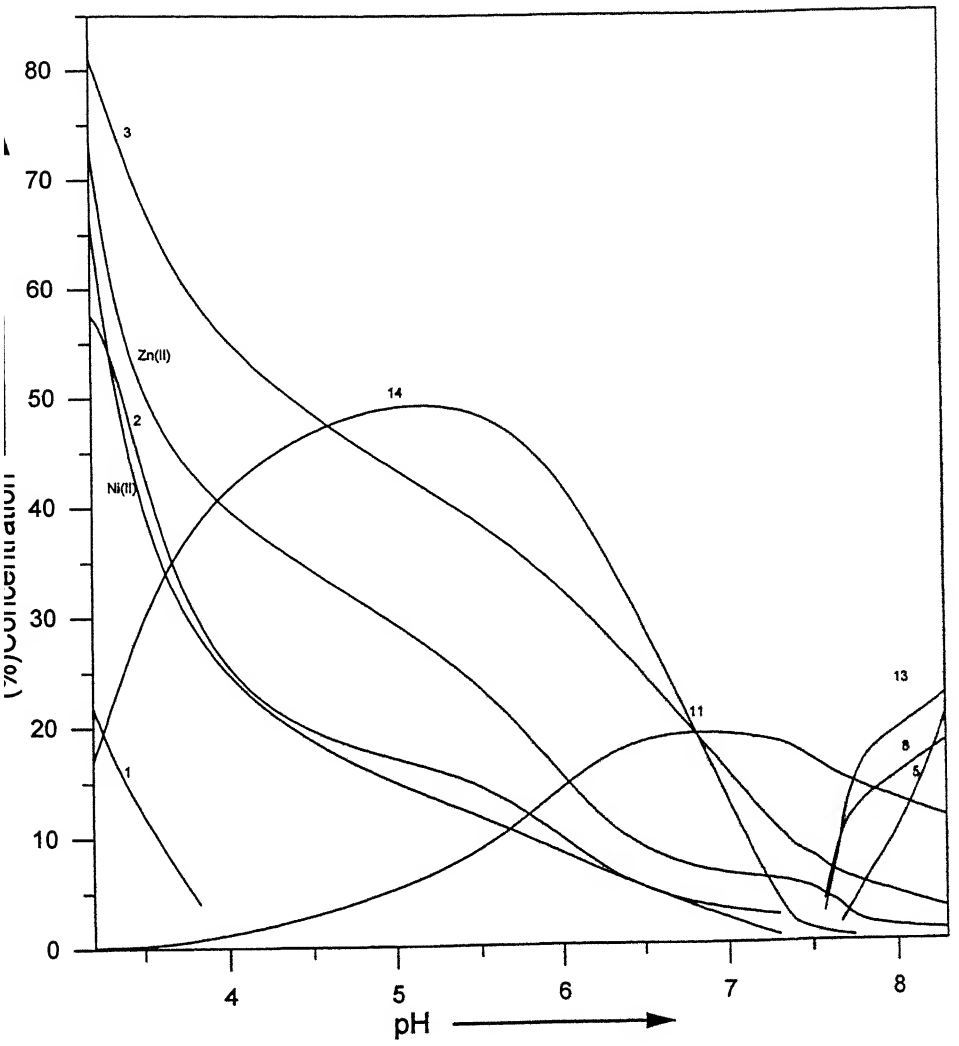



Fig.4.78- Distribution Curves of 1:1:1:1 Ni(II)-Zn(II)-Asparagine-Thymine system; (I) $AH_2$ (2) AH (3) BH (4) $Ni(OH)^+$ (5) $Ni(OH)_2$ (6) $Zn(OH)^+$ (7) $Zn(OH)_2$ (8) NiA (9) NiB (10) ZnA (11) ZnB (12) NiAB (13) ZnAB (14) NiZnAB

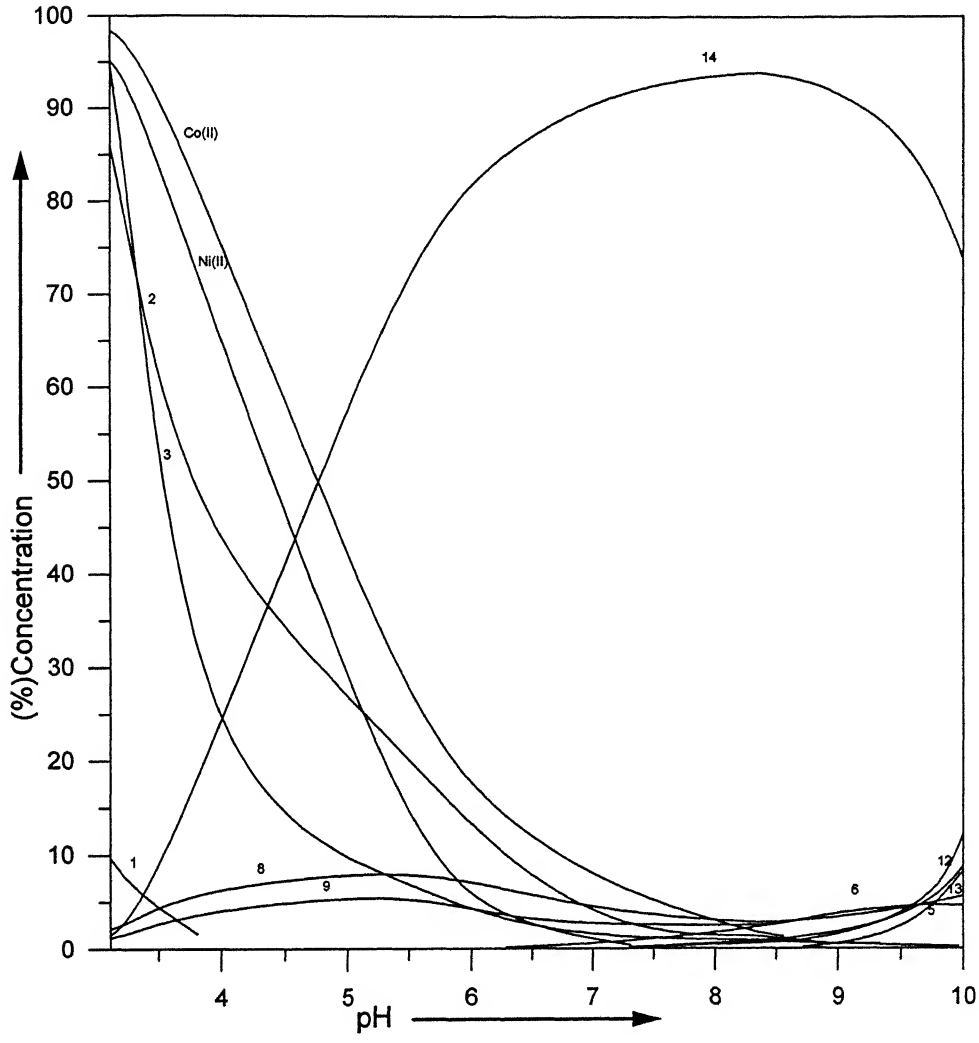



Fig.4.79-Distribution Curves of 1:1:1:1 Ni(II)-Co(II)-Asparagine-Thymine system;(I) $AH_2$ (2) AH(3) BH (4) $Ni(OH)^+$ (5) $Ni(OH)_2$ (6) $Co(OH)^+$ (7) $Co(OH)_2$ (8) NiA (9) NiB (10) CoA (11) CoB (12) NiAB (13) CoAB (14) NiCoAB

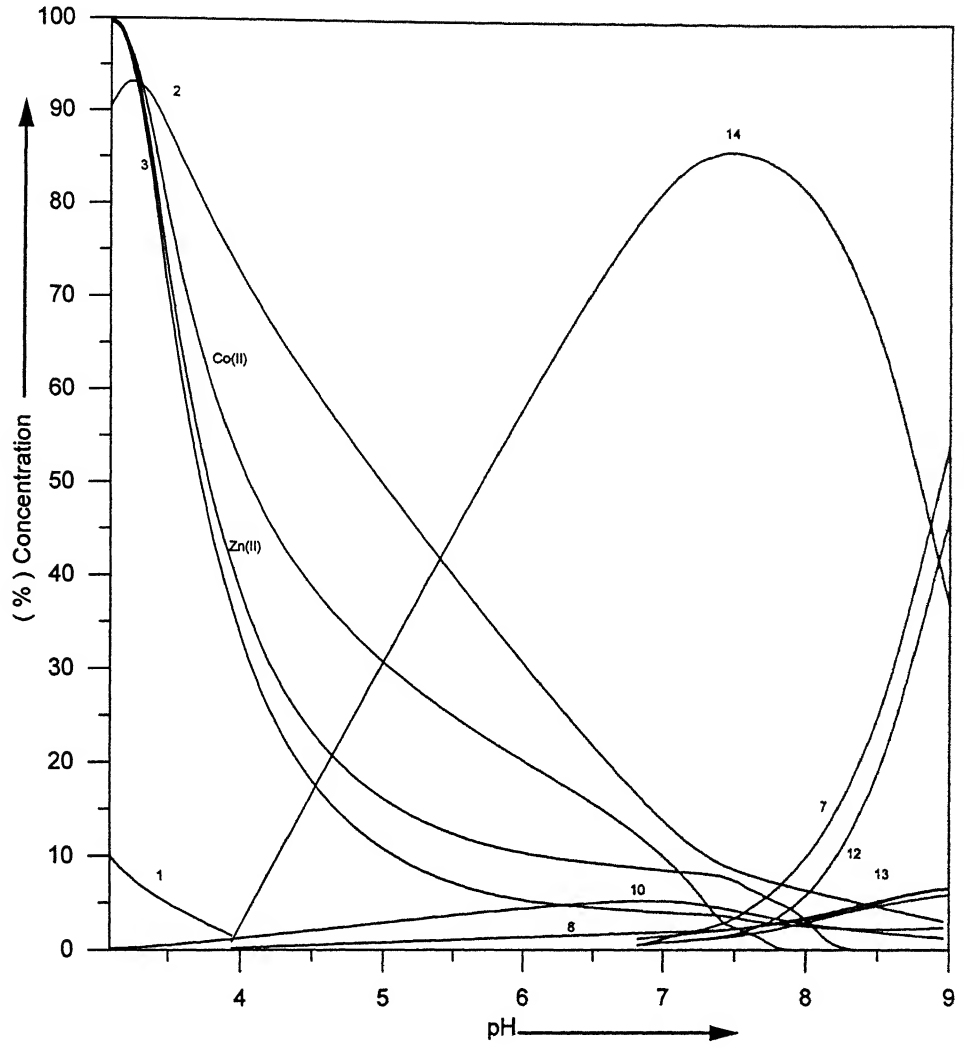



Fig.4.80-Distribution Curves of 1:1:1:1 Zn(II)-Co(II)-Aspragine-Thymine system; (I) $AH_2$ (2) AH(3) BH (4) $Co(OH)^+$ (5) $Co(OH)_2$ (6) $Zn(OH)^+$ (7) $Zn(OH)_2$ (8) ZnA (9) ZnB (10) CoA (11) CoB (12) ZnAB (13) CoAB (14) ZnCoAB

# Chapter 5

# *Conclusion*

# Conclusion

The present chapter deals with the relative stability and probable structures of binary, ternary and quaternary complexes. As discussed earlier, in preceding chapters the potentiometric equilibrium measurements in aqueous medium indicate the formation of $M_1A$, $M_2A$, $M_1B$, $M_2B$, $M_1AB$, $M_2AB$ and $M_1M_2AB$ type of complexes involving Lysine/Proline/Valine/ Asparagine as primary ligands (A) and Uracil/Thymine as secondary ligands (B) with Cu(II), Ni(II), Co(II) and Zn(II) dipositive metal ions.

The stability of ternary and quaternary complexes have been evaluated by the following equilibrium:

$$pM_1 + qM_2 + rL_1 + sL_2 + tOH \rightleftharpoons M_{1p}\,M_{2q}\,L_{1r}\,L_{2s}\,OH_t \quad (1)$$

where, $M_1$ and $M_2$ are two different metal ions, $L_1$ and $L_2$ are two different ligands taken understudy.

The global stability constant for the quaternary complexes may be represented as following:

$$\log \beta_{pqrst} = \frac{[M_{1p}M_{2q}L_{1r}L_{2s}OH_t]}{[M_1]^p[M_2]^q[L_1]^r[L_2]^s[OH]^t} \quad (2)$$

It is also possible to define the stability constants for ternary complexes in relation to their binary ones[126], represented by the equilibria (3) & (4):

$$M + B \rightleftharpoons MB \quad K^M_{MB} = [MB] / [M]\,[B] \quad (3)$$

$$MA + B \rightleftharpoons MAB \quad K^{MA}_{MAB} = [MAB] / [MA]\,[B] \quad (4)$$

The difference between the stability of the ternary and binary complexes shows the tendency of the formation of ternary species.[126] This could be expressed by Eq.(5):

$$\Delta \log K = \log K^{MA}_{MAB} - \log K^{M}_{MB}$$

$$= \log K^{MB}_{MBA} - \log K^{M}_{MA} \qquad (5)$$

The constants were refined using the SCOGS computer program[36] and the speciation as a function of pH, using ORIGIN program.

In the course of complex formation, $H^+$ ions are eventually being replaced by metal ions one at a time, so it comprises of a series of equilibria. Each equilibrium has equilibrium constants $K_1$, $K_2$, $K_3$.....$K_n$, depending on number of equilibria. The overall stability constant is simply the equilibrium constant for the total reaction found by multiplying together all the individual values of $K_1$, $K_2$, $K_3$.....and so on.

The protonation constants of ligands, overall stability constants of binary, ternary and quaternary complexes described in chapter IV have been compiled together and rearranged in Table 5.1, 5.2, 5.3 & 5.4. The stability constants of quaternary systems fall in the following orders:

(1) [Proline – Uracil – $M_1$ – $M_2$] Systems

Cu – Ni > Cu – Zn > Cu – Co > Ni – Zn > Ni – Co > Co - Zn

(2) [Lysine – Uracil – $M_1$ – $M_2$] Systems

Cu-Ni > Cu-Zn > Cu-Co > Ni-Zn > Ni-Co> Co-Zn

(3) [Valine – Thymine – $M_1$–$M_2$] Systems

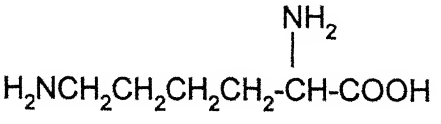
Cu-Ni > Cu-Zn > Cu-Co > Ni-Zn > Ni-Co > Co-Zn

(4) [Asparagine – Thymine – $M_1$– $M_2$] Systems

Cu-Ni > Cu-Zn > Cu-Co > Ni-Zn > Ni-Co > Co-Zn

Metals having higher logβ value of metal$L_1$ complex will be the first to attach with ligand $L_1$ which further attaches to another ligand $L_2$ to satisfy its coordination number. Coordination sites of ligands still left free will then be occupied by another metal ion. In all the binary, mixed ligand and mixed-metal mixed-ligand systems of present study following possibilities for the binding of ligands with various metal ions taken understudy may be deduced:

The **Lysine** dianion offers to an incoming ligand both a functional group which is a potential hydrogen bond acceptor, the coordinated carboxylate oxygen and two primary amine groups which are potential hydrogen bond donor. Thus, Lysine is a potentially tridentate ligand. Its structure is shown below:

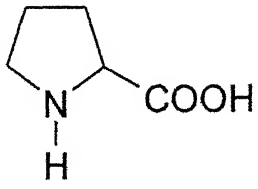


The side ∈-$NH_2$ group of the lysine residue in peptides and proteins is one of the potential donor sites for metal especially copper ion complexation. However, its coordination to the metal centre generally involves the formation of unusually large chelate rings. This fact, together with its high pK value, makes ε-$NH_2$-Cu(II) bond formation unfavourable at neutral or acidic pH[179]. The same is true for lysine itself.[180] On the other hand, in the alkaline pH range, metal ions become more competitive with respect to protons: ∈-$NH_2$ coordination in binuclear complexes of Cu(II) and oligopeptides has been reported, both in solution[181-183] and in the solid state.[184] A case of special interest is represented by the human liver-cell growth factor glycyl-histidyl-lysine found in human plasma at a concentration of about 200 $mgm^{-1}$.[185]

The most basic group is the ∈-amino group of the lysine; the terminal amino group is less basic than the ∈-amino group of the lysine residue, due to

the proximity of the electron-withdrawing carbonyl group of the peptide bond.

**Proline**




L-Pyrolidine-2-carboxylic acid (proline)

Fully protonated form of ligand proline ($\beta^-$) is represented by $H_2B^+$. It usually functions as bidentate ligand, using one carboxyl and one imino group for coordination. The pK values are 3.42 and 9.37 corresponding to the successive deprotonation of -COOH and -NH groups. Proline has one replaceable proton and behaves as monobasic acid. Its protonation equilibrium are given below:

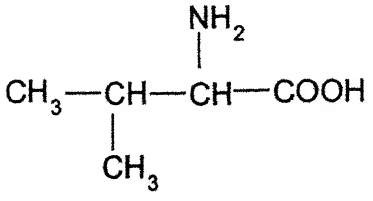
$$B^- + H^+ \rightleftharpoons HB \qquad pK_1$$

$$HB + H^+ \rightleftharpoons H_2B^+ \qquad pK_2$$

Protonation constants for the ligands have been determined by Irving-Rossotti titration technique[162] and are presented in Table 4.1. Values of protonation constants are in fair agreement with the values reported in literature.[154]

**Valine**

The structure of valine is shown below:

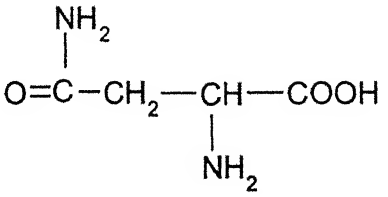


Much interest has been shown in the chemistry of β-lactam antibiotics in relation to their useful biological activities in recent years. It is known that antibiotic activity is related to the ability of these compounds to form complexes with metal ions. Gycine and valine have been preferred as ligands because they are important chelating agents. Glycine and valine form chelated compounds with various bivalent and trivalent metal ions.

Valine itself usually functions as a bidentate ligand coordinating through $COO^-$ and N atom. The pK values 9.49 and 2.26 indicate the overall stability constant of the ligand.[154]

**Asparagine**

The structure of Asparagine is shown below:

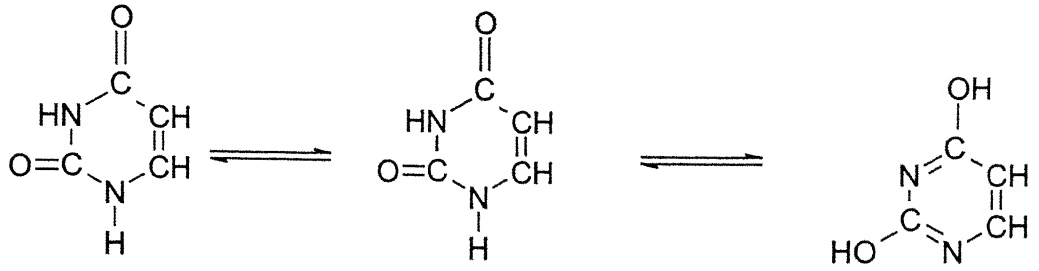


Coordinating through one amino group and one carboxylate O atom.

By using near UV circular dichroism (CD) and solvent proton nuclear magnetic relaxational dispersion measurement three different conformational states have been detected in $Ca^{2+}$ - $Mn^{2+}$ - conconavalin. A upon binding a variety of Asparagine – linked carbohydrates. (Bhattacharya et al.).[186]

**Uracil**

Uracil, a pyrimidine undergoes keto enol tautomeric shifts because of its resonance structure due $-NH_2$ and –OH substrant. The keto tautomer referred as the lactum structure while the enol tautomer is referred as lacting structure.



Lactam Lactam Double Lactam

Infra red and ultra violet spectral studies have shown that uracil exists in diketo structure. Proton ionization from uracil in the strongly acid region (pK < 0.5) has been reported based on spectrophotometric data. Levene, Bass and Simme observed that uracil has two ionizable protons, yet they yield only one pK value i.e. 9.45, whereas Srivastavas obtained its value 9.16 at 30°C and 0.1M ($NaClO_4$) ionic strength. Sugar and fox spectrophotometrically reported two pK value 9.5 and 13. On the basis of UV measurements in aqueous solution, uracil exists primarily in the diketo form whereas in alkaline solution, it exists as approximately 1:1 mixture of the two possible deprotonated form. Two overlapping absorption bands with λ-max 260 and 284 nm have been reported for proton ionization from neutral uracil with a conclusion that protons ionize simultaneously from both $N_1H$ and $N_3H$ groups.

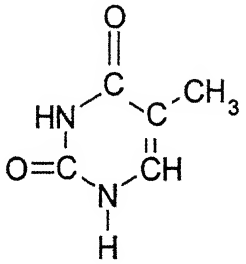
The formation and stability of some metals complexes of nucleic acid bases have been potentiometrically investigated by Freiser. Liutan and Back studied the interaction of transition metal with uracil in aqueous solution and suggested that the possible coordination site in the ligand was $N_3$.

In Ni(II), Co(II) and Zn(II) complexes uracil[187] acts as a monodentate ligand coordinating through only one nitrogen, but in the Cu(II) complex, it is bidentate coordinating through carbonyl oxygen and nitrogen. Crystallographic studies have earlier shown that mercury binds to $O_4$ in

occurs at $N_3$ position, which has also been observed by Berger and Eichharn in the NMR study of Cu(II)-cytidine. Thus, on an analogy, it would be reasonable to assume that in present complexes, $N_3$ and $O_4$ of the carbonyl group.

**Thymine**

Thymine (5-methyl uracil) is chemically 2,4-dioxo-5methyl pyrimidine. Thymine is unique among the nucleic acid constituents, in that there are no free lone pairs available for metal complexation. In fact, solution and preparative studies indicate that except for $Hg^{2+}$ and $RHg^{+}$, the interaction between transition metal complexes and thymidine is weak (Marzilli, 1977). In a copper(II) complex of thymine; the metal binding site is N(1) and the base is in its monoanionic form.



Thymine

Proton ionization from thymine in the strongly acid region (pH < 0.5) has been reported, based on spectrophotometric data. This ionization is apparently from a cationic species, but no definite information regarding ionization site or pK value is available. Levene, Bass and Simms observed that although theoretically thymine has two ionisable protons, yet it yields only one pK value, they reported the pK value of thymine as 9.9 whereas Srivastava obtained its value 9.70 at 30°C and 0.1M ($NaClO_4$) ionic strength.

Shugar and Fax spectrophotometrically determined the two pK values for thymine 9.9 and >13.

It has been concluded that in general thymine acts as a bidentate ligand.[188] In Cu(II) and Co(II) complexes coordination occurs through the ring nitrogen and carbonyl oxygen, whereas in Ni(II) complex bonding occurs from both the ring nitrogens. In the Zn(II) complex also bonding occurs from ring nitrogen and one carbonyl oxygen but one thymine coordinates at $C_2O$ position, whilst the other does at $C_4O$.

Mixed ligand complexes of metal-adenosine-thymine are of special significance from biological point of view. Since these pairs form complementary pairs in DNA and RNA respectively.

The dissociation of proton from thymine is form $N_3H$ group[189,190]. Since thymine is the nucleoside of thymine, so, it may be assumed that the first dissociation from thymine is from $N_3H$ group. Thymidine shows only single dissociation since hydrogen in $N_1$ positon of the pyrimidine is substituted by sugar moiety.[191]

Regarding the binding sites in thymidine NMR studies of Hiroyuki[192] et. al. indicates that thymidine binds to the metal ion through the $N_3$ is the probable binding site in the corresponding base. The stability constant of 1:1 metal thymidine system follow Irving Williams order of stability.

The extra stabilities of ternary complexes should be due to hydrophobic or stacking interactions of the ligands. Taqui Khan and Satyanarayan have already reported the stacking interactions between Adenine-Thymine and Adenine-Uracil systems.

A perusal of the distribution diagram reveals that at very low pH the concentration of mixed ligand complexes are less than those of protonated ligands. As the pH increased the concentrations of the ternary species

increased. In the case of copper complexes the concentration of the ternary species are more than even those of the ligand species.

The extra stability of the ternary complexes are due to the interactions outside the coordination sphere. This may sometimes be the formation of hydrogen bonds between the coordinated ligands. A similar stabilizing effect may likewise be exerted by the electrostatic interactions between non-coordinated, charged groups of the ligands Sakuri et al[193-196] carried out extensive studies to establish the laws governing interactions of this nature.

The marked stabilization of the ternary relative to the binary complexes is reflected in the species-distribution plots, i.e., the ternary complexes occur in larger concentrations than the binary complexes in each of the systems studied. Similarly, the quaternary complexes occur in larger concentrations than the ternary complexes.

**Future Scope**

Considerable attention has been focused on the binding of metal ion and metal chelates to pyrimidines. Besides throwing light on the formation of mixed-metal, mixed-ligand complexes, the present work offers further scope of a fruitful future work which would profitably be directed to the following.

(1) Solid state synthesis, characterization including x-ray analysis of these chelates may be carried out.

(2) A part from equilibria studies, the structural interactions of the multimetal-multiligand complexes may be studied by viscometric, volumetric analysis, surface tension and ultrasonic velocity measurements.

(3) Biological activity of the multinuclear chelates may be carried out.

(4) Heavy metal complexes can be used for isomorphic replacement in x-ray crystallographic studies of t-RNA and for sequencing investigations by electron microscopy.

**Table 5.1**

**Stability constants and other related constants of binary, ternary and quaternary complexes of Lysine (A) and Uracil (B) with different metal ions in aqueous solution at 37±1°C, I = 0.1 M $NaNO_3$.**

(A) Proton-ligand formation constants ($\log \beta_{oorst}$)

| | |
|---|---|
| $AH_3$ | 21.84 |
| $AH_2$ | 19.77 |
| AH | 10.69 |
| BH | 9.47 |

(B) Hydrolytic constants ($\log \beta_{porot}$)

| Complex | Cu | Ni | Zn | Co |
|---|---|---|---|---|
| $M(OH)^+$ | -6.29 | -8.10 | -7.89 | -8.23 |
| $M(OH)_2$ | -13.10 | -16.87 | -14.92 | -17.83 |

(C) Metal-ligand constants ($\log \beta_{porst}$): Binary systems

| Complex | Cu | Ni | Zn | Co |
|---|---|---|---|---|
| M-A | 11.56 | 8.30 | 8.22 | 6.12 |
| M-B | 8.25 | 6.80 | 6.61 | 6.28 |

(D) Metal-ligand constants ($\log \beta_{porst}$): Ternary Systems

| Complex | Cu | Ni | Zn | Co |
|---|---|---|---|---|
| M-A-B | 15.54 | 12.64 | 11.24 | 11.63 |

(E) Metal-ligand constants ($\log \beta_{pqrst}$): Quaternary systems

| Complex | Cu-Ni | Cu-Zn | Cu-Co | Ni-Zn | Ni-Co | Zn-Co |
|---|---|---|---|---|---|---|
| $M_1M_2$-A-B | 23.40 | 23.28 | 22.25 | 21.55 | 19.15 | 18.85 |

**Table 5.2**

**Stability constants and other related constants of binary, ternary and quaternary complexes of Proline (A) and Uracil (B) with different metal ions in aqueous solution at 37±1°C, I = 0.1 M $NaNO_3$.**

(A) Proton-ligand formation constants (log $\beta_{oorst}$)

| | |
|---|---|
| $AH_2$ | 12.79 |
| AH | 9.37 |
| BH | 9.47 |

(B) Hydrolytic constants (log $\beta_{porot}$)

| Complex | Cu | Ni | Zn | Co |
|---|---|---|---|---|
| $M(OH)^+$ | -6.29 | -8.10 | -7.89 | -8.23 |
| $M(OH)_2$ | -13.10 | -16.87 | -14.92 | -17.83 |

(C) Metal-ligand constants (log $\beta_{porst}$): Binary systems

| Complex | Cu | Ni | Zn | Co |
|---|---|---|---|---|
| M-A | 8.04 | 6.39 | 5.60 | 5.83 |
| M-B | 8.25 | 6.80 | 6.61 | 6.28 |

(D) Metal-ligand constants (log $\beta_{porst}$): Ternary Systems

| Complex | Cu | Ni | Zn | Co |
|---|---|---|---|---|
| M-A-B | 16.51 | 11.66 | 11.40 | 11.54 |

(E) Metal-ligand constants (log $\beta_{pqrst}$): Quaternary systems

| Complex | Cu-Ni | Cu-Zn | Cu-Co | Ni-Zn | Zn-Co | Ni-Co |
|---|---|---|---|---|---|---|
| $M_1M_2$-A-B | 23.35 | 23.15 | 22.84 | 19.68 | 19.15 | 19.61 |

**Table 5.3**

**Stability constants and other related constants of binary, ternary and quaternary complexes of Valine (A) and Thymine (B) with different metal ions in aqueous solution at 37±1°C, I = 0.1 M $NaNO_3$.**

(A) Proton-ligand formation constants (log $\beta_{oorst}$)

| | |
|---|---|
| $AH_2$ | 11.75 |
| AH | 9.49 |
| BH | 9.94 |

(B) Hydrolytic constants (log $\beta_{porot}$)

| Complex | Cu | Ni | Zn | Co |
|---|---|---|---|---|
| $M(OH)^+$ | -6.29 | -8.10 | -7.89 | -8.23 |
| $M(OH)_2$ | -13.10 | -16.87 | -14.92 | -17.83 |

(C) Metal-ligand constants (log $\beta_{porst}$): Binary systems

| Complex | Cu | Ni | Zn | Co |
|---|---|---|---|---|
| M-A | 8.11 | 5.42 | 4.86 | 4.45 |
| M-B | 8.83 | 8.20 | 7.06 | 6.34 |

(D) Metal-ligand constants (log $\beta_{porst}$): Ternary Systems

| Complex | Cu | Ni | Zn | Co |
|---|---|---|---|---|
| M-A-B | 15.33 | 12.81 | 11.62 | 11.31 |

(E) Metal-ligand constants (log $\beta_{pqrst}$): Quaternary systems

| Complex | Cu-Ni | Cu-Zn | Cu-Co | Ni-Zn | Ni-Co | Zn-Co |
|---|---|---|---|---|---|---|
| $M_1M_2$-A-B | 23.00 | 21.25 | 20.16 | 19.55 | 17.29 | 18.15 |

We have confined our discussion to transition metal centers, copper(II), nickel(II) cobalt(II) and zinc(II).

In aqueous solutions $Cu^{2+}$ ($d^9$) is tetragonally coordinated by six water molecules. Two axial water molecules lie at longer distances from the copper and are more labile than the four other water molecules.

The hydrated nickel ion presents regular octahedral configuration. Six equivalent sites of coordination are available unless a stronger ligand field provokes a tetragonal distortion and ultimately a square planar configuration. Hexacoordinated nickel is expected to form a greater number of isomeric complex species than copper, whose coordination geometry is usually dominated by the four "equatorial bonds".

The configuration of zinc can easily move from tetrahedral geometry to octahedral geometry depending upon the nature of bound ligands[197]. Consequently the possible mixed species are in greater number than with copper.

The cobalt (II) chelate of the dipeptide glycylglycine was also found to absorb oxygen reversibly[198]. This field has been recently reviewed by Wilkins.[199] There examples tend to show that oxygen absorption is a specific property of cobalt complexes.

The solution structures of the various ligands and the probable structure of the chelates in solution are shown in figures 5.1-5.19.

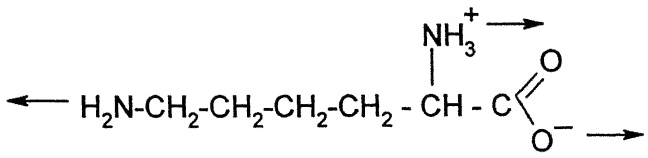


Fig. 5.1: Solution structure of Lysine (Lys).

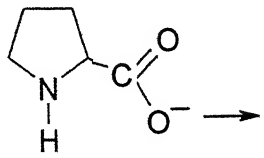


Fig. 5.2: Solution structure of Proline (Pro).

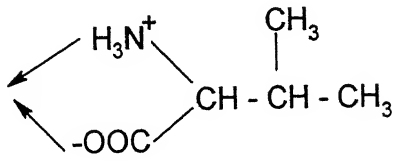


Fig. 5.3: Solution structure of Valine (Val).

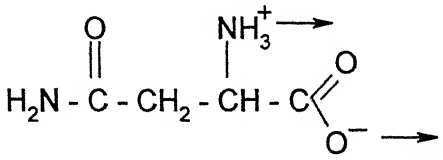


Fig. 5.4: Solution structure of Asparagine (Asp).

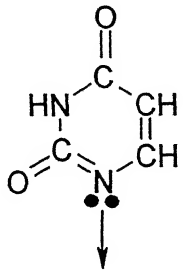


Fig. 5.5: Solution structure of Uracil (Ura).

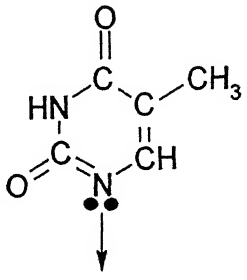


Fig. 5.6: Solution structure of Thymine (Thy).

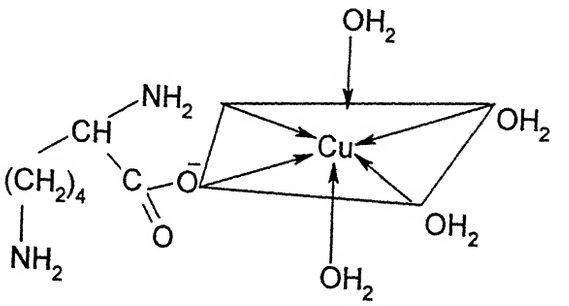



Fig. 5.7: Proposed structure of Binary Cu(II)-Lysine.

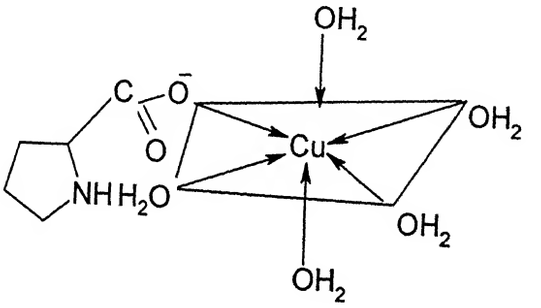



Fig. 5.8: Proposed structure of Binary Cu(II)-Proline.

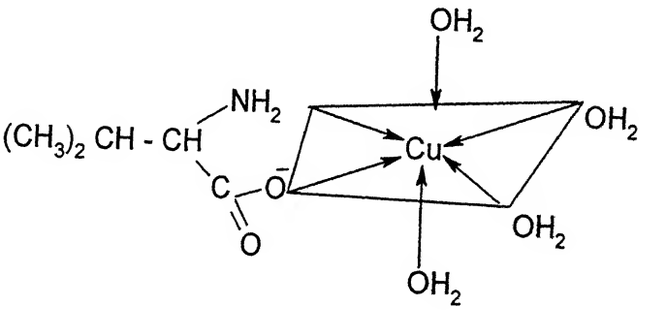



Fig. 5.9: Proposed structure of Binary Cu(II)-Valine.

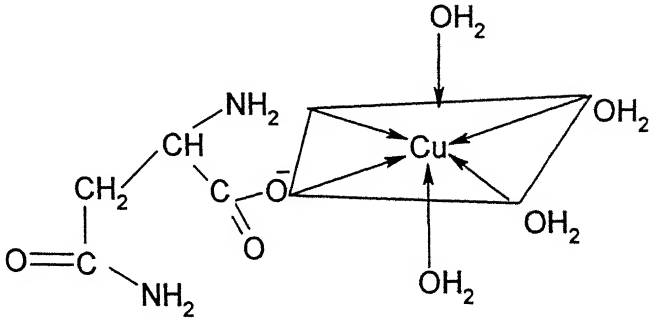



Fig. 5.10: Proposed structure of Binary Cu(II)-Asparagine.

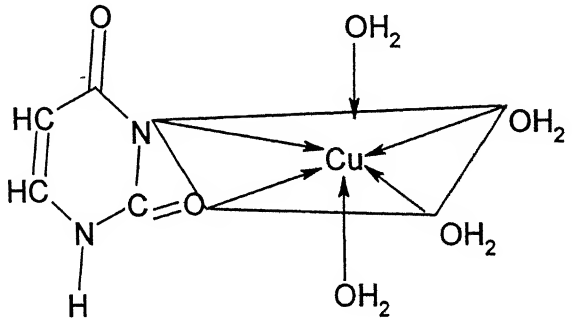



Fig. 5.11: Proposed structure of Binary Cu(II)-Uracil.

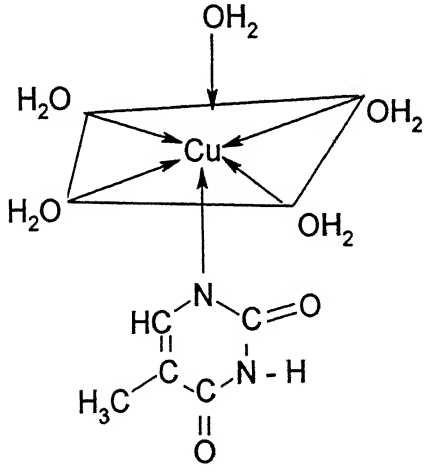



Fig. 5.11: Proposed structure of Binary Cu(II)-Thymine.

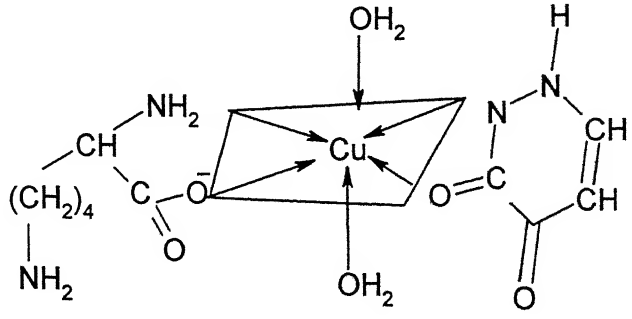



Fig. 5.12: Proposed structure of Ternary Cu(II)-Lysine-Uracil.

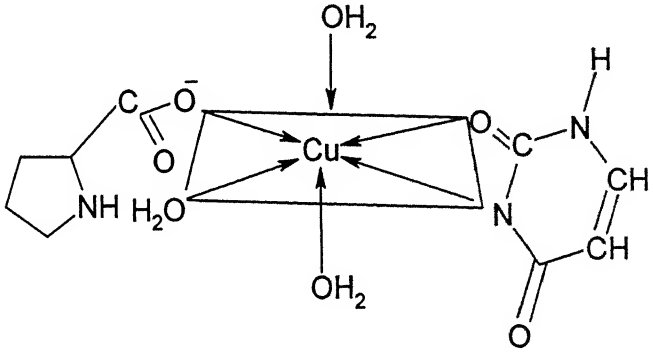



Fig. 5.13: Proposed structure of Ternary Cu(II)-Proline-Uracil.

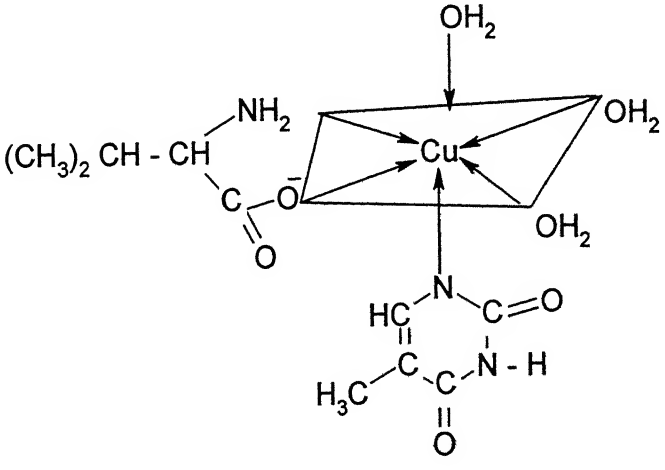



Fig. 5.14: Proposed structure of Ternary Cu(II)-Valine-Thymine.

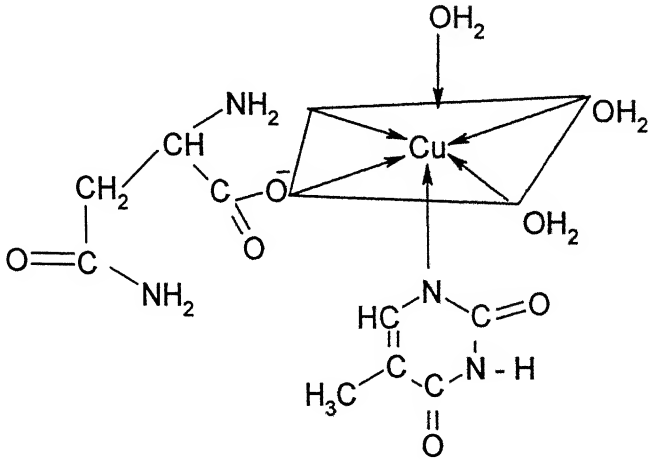



Fig. 5.15: Proposed structure of Ternary Cu(II)-Asparagine-Thymine.

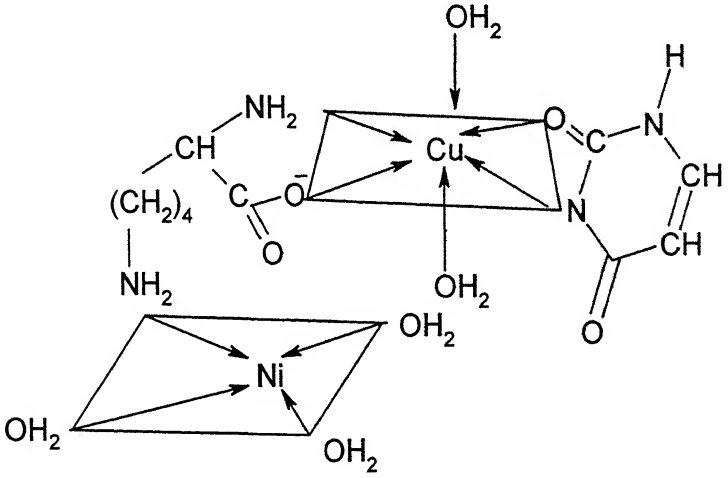



Fig. 5.16: Proposed structure of Quaternary Cu(II)- Ni(II)-Lysine-Uracil.

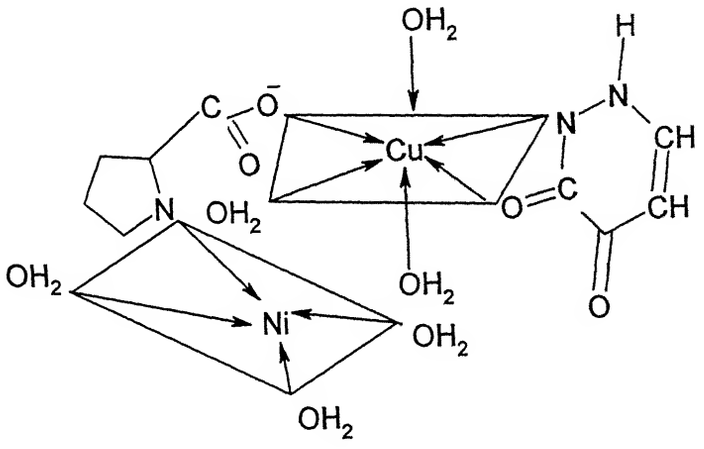



Fig. 5.17: Proposed structure of Quaternary Cu(II)- Ni(II)-Proline-Uracil.

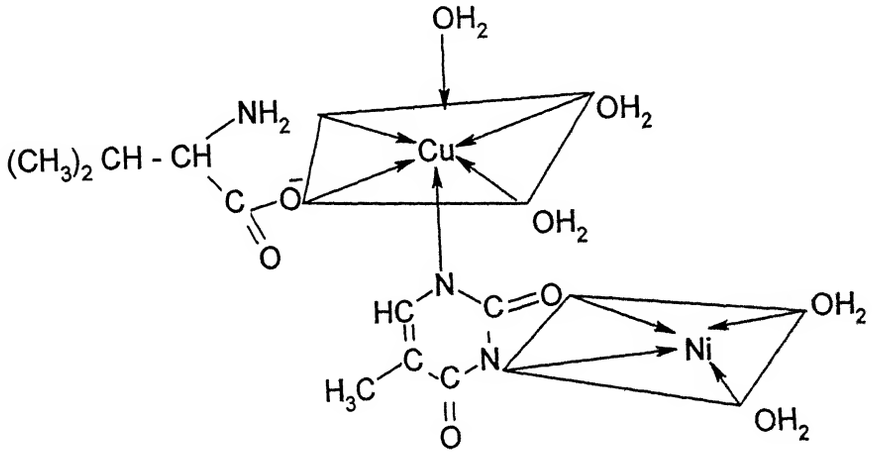



Fig. 5.18: Proposed structure of Quaternary Cu(II)-Ni(II)-Valine-Thymine.

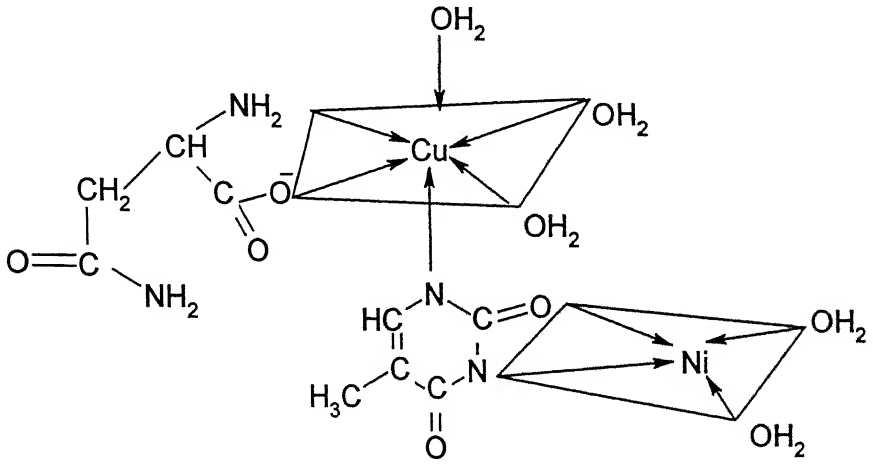



Fig. 5.19: Proposed structure of Quaternary Cu(II)-Ni(II)-Asparagine-Thymine.

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